MINERALOGY AND PHYSICAL PROPERTIES OF SOME TASMANIAN CAINOZOIC CLAYS

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ABSTRACT

Detailed quantitative mineralogical analysis and physical studies were made of twenty nine Cainozoic clays from different parts of Tasmania. The clays are mainly of Tertiary age and are both residual and sedimentary in origin. The geological occurrences of the clays are described and their mineralogy discussed. The two main methods of analysis consisted of X-ray diffraction techniques and differential thermal analysis; iron determinations were made on four selected samples. The differential thermal method of analysis in conjunction with X-ray diffraction examination proved advantageous in detecting an abnormal montmorillonite which was characterised by a lower dehydroxylation peak at about 550°C.

The clays can be divided into five types, on the basis of their most abundant clay mineral, as follows:

1. Clays rich in kaolinite
2. Clays having abnormal montmorillonite as the dominant clay mineral.
3. Clays characterised by mixed layer minerals of illite and montmorillonite, as both randomly stacked and ordered structures.
4. Clays characterised jointly by kaolinite and abnormal montmorillonite.

5. Clays predominantly kaolinites with gibbsite.

Quartz was abundant in all the clays. Other minor constituents included; illite, feldspar, goethite, gibbsite, metahalloysite, calcite, chlorite, haematite, muscovite, mixed layer minerals and organic matter.

The clay minerals were used as indicators to interpret tentatively the environment of deposition during the Cainozoic Era. The possibility exists that different clay minerals might have formed in the weathered zones at different periods in the geological history of the area as a result of changes of micro-chemical climate. In the 36' bored at Sandy Bay the mineral composition revealed no diagenetic change with the accumulation of the clays.

Most of the clays required a high proportion of tempering water. Drying and firing characteristics were related to clay mineralogy. Of the two chief mineralogical groups, clays which consist primarily of kaolinite are of medium plasticity and shrinkage, light coloured on firing and moderately refractory. Another group of clays with abnormal montmorillonite, or mixed layer minerals have high plasticity and shrinkage, are very slow in drying, orange - red burning and low - refractory.

INTRODUCTION

This thesis was undertaken under the direction of Professor S. W. Carey, Professor of Geology, University of Tasmania, Mr. G. E. A. Hale, Geologist in Charge, Hydro Electric Commission, Hobart, and Dr. W. F. Cole, Principal Research Officer, C.S.I.R.O., Highett, Victoria.

The clay samples collected from different parts of Tasmania and analysed mineralogically do not represent the potentially valuable industrial clay deposits of any area. The majority of the clays are Tertiary lacustrine clays, a few of them are residual deposits and a bore hole was sunk to a depth of about 36 feet, to find out the clay mineral variations and diagenesis with depth, however all the clays studied are of the same general age (Cainozoic). The main objective in the present study was to obtain detailed information on the mineralogy and physical properties of the argillaceous formations of known non-marine origin and to consider where possible the significance of the clay mineralogy data in relation to environment of accumulation and any diagenetic change. Two main methods were employed in clay mineral identifications, namely, differential thermal analysis and X-ray diffraction and where possible, iron determination were also made for differentiating abnormal

montmorillonite from nontronite. Some physical properties were also studied.

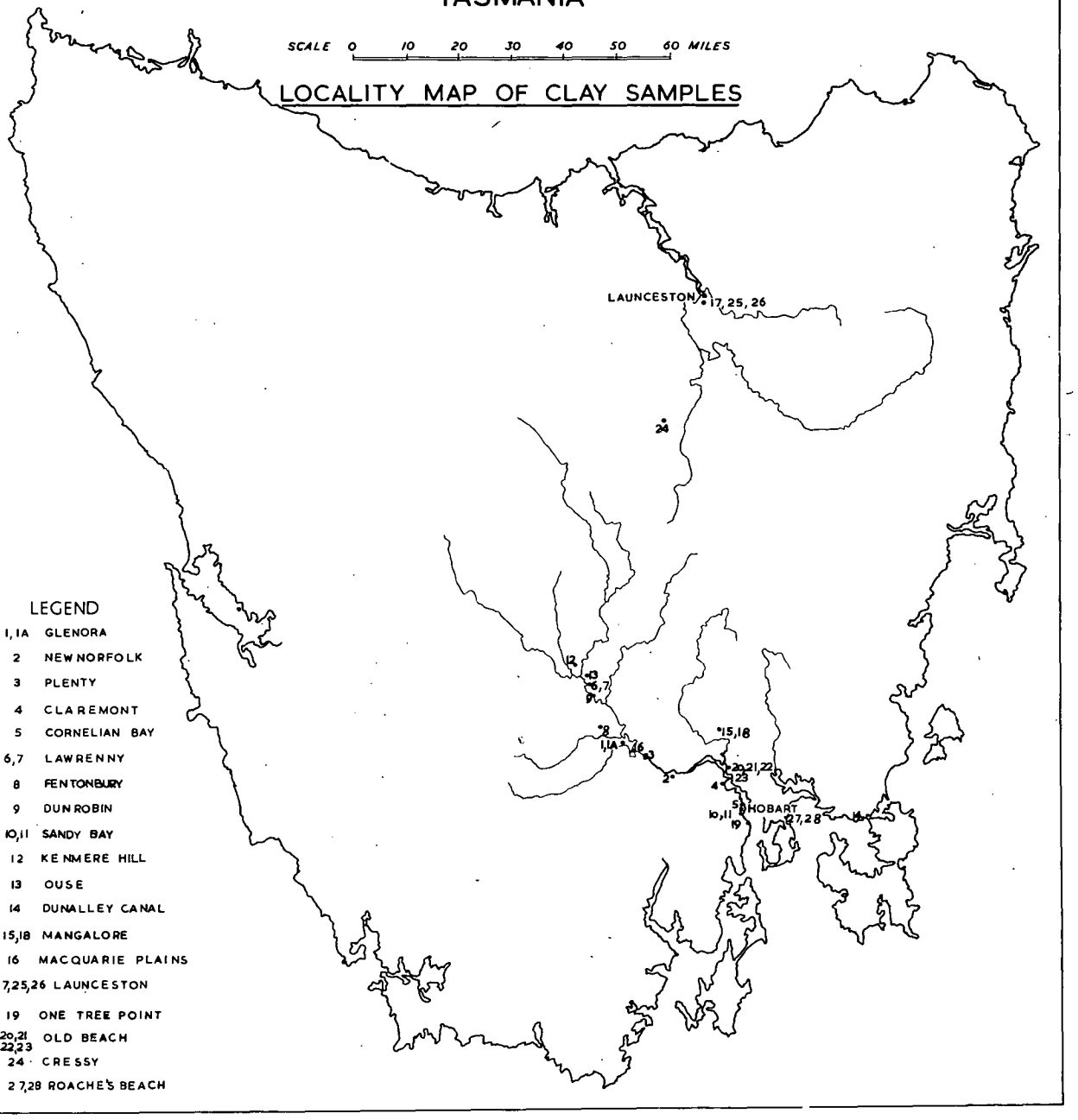
This work on the clay minerals occurring in the non - marine clays, which are of the Cainozoic Era, contributes to the relatively scanty mineralogical information on such rocks. The presence of abnormal montmorillonite in some of the clays is of additional interest.

PLATE I.

TASMANIA

SCALE 0 10 20 30 40 50 60 MILES

LOCALITY MAP OF CLAY SAMPLES



LEGEND

1, 1A	GLENORA
2	NEW NORFOLK
3	PLENTY
4	CLAREMONT
5	CORNELIAN BAY
6, 7	LAWRENNY
8	FENTONBURY
9	DUNROBIN
10, 11	SANDY BAY
12	KENMERE HILL
13	OUSE
14	DUNALLEY CANAL
15, 18	MANGALORE
16	MACQUARIE PLAINS
17, 25, 26	LAUNCESTON
19	ONE TREE POINT
20, 21, 22, 23	OLD BEACH
24	CRESSY
27, 28	ROACHE'S BEACH

GEOLOGICAL OCCURRENCE

TERTIARY LACUSTRINE SEDIMENTS

Tertiary lake clays have been examined from different parts of Tasmania. As established by Carey (1954), prolonged erosion and peneplanation was followed in the early Tertiary by an epeirogeny and strong block faulting and tilting took place thus giving rise to the deep lakes. These were rapidly filled by clastic sediments of various grade sizes derived from dolerite (Jurassic ?), Triassic and Pre-Mesozoic (?) sediments.

These rocks are most characteristically developed in the 'Launceston Tertiary basin' and earlier references to such lacustrine sediments consisting of siltstones, sandstones, gravels, conglomerates, mudstones, clays and silicified wood have been made by Johnston (1888), Edwards (1939), Carey (1946), Lewis (1946), Voisey (1948), Banks (1952) and Spry (1955).

Clay Samples No. 1 and 1A from Glenora

These clay samples were collected from the Glenora road cutting (Map. No. 4774). Overlying the basal conglomerate bed are sandstones and claystones and the individual beds range in thickness from 18 inches to 6 feet. The road cutting east of

Glenora exposes three beds below the basalts. The clay bed immediately below the basalt (Sample No. 1) is white in colour and about 6 feet thick. This bed is underlain by yellow to orange coloured claystone, 5½ feet thick, (Sample No. 1A). Both these clays contain many leaf impression and are underlain by medium to coarse grained feldspathic sandstones (of Triassic age ?).

The lake sediments of the Glenora area are probably produced by the weathering of dolerite, Triassic sandstones and Palaeozoic sediments.

Clay Sample No. 3 from Plenty

This clay sample was collected from the Plenty road metal quarry on the Lyell Highway near the old Plenty bridge (Map. No. 4873). The section is of Triassic feldspathic sandstones overlain by a sub-basaltic conglomerate tuff bed, ferruginous shale band and 2 feet of white to brown coloured sandy clay with tuff intercalations and ferruginous shale, followed by a basaltic flow.

The source rocks for the accumulation of the lake sediments of the Plenty area are probably the same as those found at Glenora, together with Tertiary volcanic rocks.

Clay Sample No. 16 from Macquarie Plains

This clay sample is from near the Macquarie Plains railway station at grid locality E482000 N742854, Map. No. 4874. The scoriaceous basaltic flow is overlain by a thin limonite concretionary zone and a lacustrine sediment 18 inches thick. The latter is white to grey in colour and contains quartz in a clayey matrix.

The clay samples from Glenora, Plenty and Macquarie Plains are from the same general area which, as established by Anandalwar (1957), formed one lake extending from Glenora to Plenty.

Clay Sample No. 2 from New Norfolk

This clay sample from the road cutting at 957336 (Hobart sheet) just east of New Norfolk is brownish in colour. Although collected for study as a Tertiary lacustrine clay it had been given a Pleistocene age (Lewis, 1934, 1936), which has not been substantiated by any fossil evidence. The only fossils found in these sediments are plant remains and opalised wood which cannot be used for establishing the correct age.

These sediments to the east of New Norfolk consisting of gravels, sands and sandy clays have been found (Wooley 1956) at a lower level than basalt, (Tertiary).

There is some evidence (Wooley 1956) to show the fluviatile rather than lacustrine nature of these sediments from a sand sample from a road cutting, just outside the town of New Norfolk, at map ref. 956336 (Hobart sheet)

This evidence is its poor sorting and the bimodality of the grades present. However the nature of clay sample No. 2 is discussed in a later chapter with relation to its clay mineralogy and environments of deposition.

Clay Sample No. 4 from Claremont, Windermere Beach

This clay sample, white in colour, was collected from the northern end of Windermere Beach. The bed exposed is only a foot in thickness. The area at Windermere Beach is occupied by river terraces, stratified sandstones and ferruginous layers of less consolidated sands.

Clay Sample No. 5 from Cornelian Bay

A bed of white clay about 3 feet thick exposed behind the Baths at Cornelian Bay, in the Derwent estuary, is overlain by sandier beds and a thin capping of soil about 3 feet thick. The outcrop is essentially an eroded mass of low topography with dolerite covered by these younger formations.

Clay Samples No. 6 and 7 from Lawrenny

These clay samples of light grey colour were collected from the irrigation canal below Mr. Brock's house and between Lawrenny wool shed and Red Point (20 feet below the irrigation canal) respectively.

The area is situated on the east side of the Derwent River, between the townships of Hamilton and Ouse. The rocks occupying the area are dolerites, basalts and Triassic sandstones and shales. In Tertiary times, thick and extensive deposits of clays, lignite and sand were laid down. Gravels, sands and white clays of Quaternary age occupy the flood - plains of the Derwent.

A log of a bore hole (E) in Mr. Brock's estate reveals a complete section of the Tertiary strata in this basin. The clay reserves in this area are probably large enough to support an industry for a 60 feet bed of clay occurs beneath a 10 feet cover of sand.

Clay Sample No. 8 from Fentonbury

This clay sample was collected from the Whiting deposit at Fentonbury and its age is unknown. It is regarded

as being residual in origin and produced by the weathering in situ of dolerite.

Clay Samples Nos. 9 and 12 from Ouse and Kenmere Hill

Sample No. 9 is from the left bank of the River Derwent near Dunrobin Bridge and about 4 miles south-east of Ouse village.

Sample No. 12, is from Kenmere Hill, Ouse, about 55 miles by road north-west from Hobart and about $2\frac{1}{2}$ miles north-north-west of Ouse village.

The area near Ouse is occupied by Triassic sandstones which have been intruded by a dolerite sill. Strong erosion has stripped the cover from the dolerite, on which later weathering developed a mantle of ferruginous bauxite (laterite). This land surface was later faulted, tilted and eroded and then buried under fresh water sediments and basaltic flows. These clays overlying the bauxite are not lake deposits but are of Tertiary age. They are primary in origin and were due to the resilication of the bauxite material. The silica was introduced from the underlying parent rock or the overlying Derwent lake beds. The clay minerals have developed at the expense of gibbsite and bauxite by kaolinization of the fresh rock beneath

the bauxite and the changed conditions checked the formation of bauxite and initiated kaolinitic weathering. The formation of gibbsite takes place under conditions in which there is a relatively high pH (i.e. alkaline conditions), the absence of any humic acid and thorough leaching. In the presence of acid humus substances, and neutral to acidic pH, the silica carrying the negative charge joins up with the alumina to form aluminium silicates.

Clay Samples Nos. 10 and 11 from Sandy Bay, University Area

A hand auger was employed to sink a bore hole to a depth of about 36 feet, behind the Geography Department, University of Tasmania, Hobart. With the equipment used it was not possible to drill to greater depths.

Samples of clay were collected at intervals of 1 foot but no significant variation in their physical characters was found in the first 20 feet. The top 20 feet is a yellowish brown clay mixed with medium to very fine sand particles (Sample No. 10)

Sample No. 11 of dark greyish clay mixed with sand and carbonized wood is from a depth between 20 and 36 feet.

These Tertiary lake sediments are the remnants of an initially more extensive deposit and are probably underlain by Permian beds and Jurassic dolerites.

Clay Samples No. 13 from Q/M.P. 105(Ouse.)

This clay sample, exposed in a road cutting was collected on the Lyell Highway, near mile post 105 from Queenstown. In this area there has been a rapid accumulation of sediments as revealed by the poor sorting and the sedimentary structures of the sub-basaltic lacustrine sediments, which consist of ferruginous sandstones and claystones (Jennings 1955). This rapid sedimentation took place by the erosion and transportation of laterite which overlay clays, dolerite, Permian rocks and Triassic sandstones. The rocks are not highly lithified and some of the sandstones contain limonitic matrix and nodules, which have been introduced through the weathering of overlying basalts.

Clay Samples No. 14 from Dunalley

This clay sample was collected from the spoil heaps from the Dunalley Canal. It is thought to be of Tertiary age, but this area has never been mapped geologically as far as is known.

Clay Samples Nos. 15 and 18 from Mangalore

In the Bagdad Rivulet valley there is a series of poorly consolidated clay and sand beds underlain by basaltic flows. The section was described by McDougall (1957).

A 5 feet bed of clay is exposed where the Rivulet has cut down through the terrace. In the Bagdad Rivulet at 118481, 15 yards north of the bridge, there occurs a bed of clay containing some coarser material characterised by a strongly weathered basalt in situ. This is overlain by 18 inches of poorly consolidated sand, followed by river gravels. The clay sample No. 15 from Mangalore was collected from a clay bed 5 yards north of the bridge.

South of the bridge at a slightly lower level, several feet of grey plastic clays occur. In the rivulet about 550 yards north of the bridge, is another 5 feet thick bed of white clay, which is overlain by river gravels. This clay forms Sample No. 18, collected from the locality, Photo 17695, Brighton run 7, station 825.

The extent of the clay deposit is not known due to the covering of river gravels and alluvium. However, the local residents believe that the clay reserves are fairly large

and this is further proved by the presence of clay in the telegraph post holes and at 117478, where petrol storage tanks have been installed. A few trenches and auger drill holes would be useful to prove the reserves.

Both these clays are post-basaltic in age and were deposited in a lake dammed behind basalt.

Clay Sample No. 19, from One Tree Point, Hobart

This clay sample was collected from the road cutting at One Tree Point, Lower Sandy Bay, about three miles south of Hobart. The Tertiary lacustrine bed consists of a boulder bed and white mudstone. The latter has well developed bedding and contains poor plant fossils. Spry (1955) has shown that the mudstone is poorly sorted and closely resembles the matrix of the boulder bed. It is mainly composed of clay grade with 10 per cent of sand and 40 per cent of silt grade and probably originated from the rapid erosion of debris from steep fault scarps. The boulder bed and mudstone bed are overlain by alkali-basalt and basic pyroclastics.

Clay Samples No. 17, 25 and 26 from the Launceston area

Tertiary lacustrine clays of medium to good plasticity

occur in the vicinity of Launceston, and they belong to the Lower Tertiary Launceston Series. The sedimentation in this series varied a great deal, for the sediments include coarse boulder beds of dolerite and seams of lignite and the rest of the Tertiary sequence consists of different clays of white, cream, grey, pink and mottled colours, bedded clays and mudstone, often interbedded with soft sandstones and ferruginous shales. The clays have originated (Carey 1946) from the stripping and denudation of the under clay layer which had been developed below the laterite and bauxite crust of the old peneplain. Tertiary plant fossils indicate that the sediments of the Launceston Series accumulated in a warmer and much more humid climate than at present day.

Clay samples No. 25 and 26 are of sub-surface weathered type and are cream and light yellow in colour respectively. Both of them are used by the Campbell Pottery works, Launceston, in the manufacture of heavy clay ware and sewer pipes.

Clay sample No. 17 is used by the Huttons Brickwork, Launceston, in the manufacture of light coloured building bricks.

Clay Sample No. 24 from the Brumby Creek area, Cressy

This clay sample was collected in a southward flowing gully, about a mile E N E of the junction of the Palmerston and Billopp Roads, just off the north edge of the photograph of the Great Lake, Run 11, photo No. 4267.

The dominant rock is dolerite intruded into Triassic and Permian sediments. Following the intrusion of dolerite, a period of peneplanation produced a lateritised surface. It was succeeded by epeirogeny, faulting and erosion and the products of erosion of these rocks formed extensive lake deposits of clays, sands, and gravels, known as the Launceston Group of Tertiary sediments.

Clay Samples No. 20, 21, 22 and 23 from Old Beach

Clay samples No. 20 and 21 were collected from the creek on the Old Beach Road, where the thickness of each of the two beds in the exposed section is about 2 feet. Sample No. 20 is from the top bed, whilst sample No. 21 is from the lower sandier bed.

Clay samples No. 22 and 23 were taken from the west of the road junction between the Back Old Beach Road and Old Beach

Road. These clays are practically the same as 20 and 21.

The country around Old Beach is occupied by sandstones and mudstones; but their distribution is obscured by the soil covering. The country, rising between 200 - 400 feet, has been dissected, and is underlain by dolerite, and basalt. The geology of this area is the same as described for samples No. 27 and 28.

The clays were collected from the lacustrine sediments which overlap the basalts (Personal communication from G. E. A. Hale).

Clay Samples No. 27 and 28 from Rokeby

These clay samples of dark greyish and yellowish brown colour respectively were collected from Rokeby, about 2 miles from the main Ralphs Bay Neck turn off towards Roaches Beach. The area in the vicinity of Rokeby is occupied by rocks of the Permian System comprising of siliceous white mudstones interbedded with some sandstones and limestones. The rocks of the Triassic System are sandstones and mudstones and have been largely removed by denudation. Both these sedimentary rocks were intruded by dolerite. The younger Teritary sedimentary formations consist of horizontally bedded clays, unconsolidated

sandstone, gravels and grits, which are characterised by fossils of leaves, wood and fresh-water shells reflecting the lacustrine nature of sedimentation.

PREPARATION OF SAMPLE

This chapter deals with the technique of preparation of the clay material for mineralogical analysis.

The first part deals with the usual sedimentation method to remove the clay fraction, and the second with the 'Oriented aggregate technique' (Nagelschmidt 1941), for X-ray analysis.

Clay is used as a rock term and also as a particle size term in the mechanical analysis of sedimentary rocks and soils (Grim 1953). Generally clay implies a natural, earthy, fine grained material which develops plasticity when mixed with water. As a particle-size term, the clay fraction is composed of the smallest particles, with an upper limit variously set as 5, 2 or 1 micron, though most generally at 2 microns. The maximum size of particles in the clay grade has been defined differently by different workers. In geology, it is common practice to follow the 'Wentworth scale' (Wentworth 1922), where the clay grade is finer than about 4 microns. The soil scientists keep 2 microns as the upper limit of the clay size grade. It has also been found that the larger clay mineral particles break down easily to 2 microns, when the clay

is slaked in water. The analyses have shown that the non-clay minerals are usually absent in particles smaller than about 1 to 2 microns, therefore a separation of 2 microns fraction is important and has been followed in this work for removing the clay grade from the clay materials.

It is physically impossible to analyse an entire outcrop of clay or any other sedimentary formation. The sampling of the clay was done very carefully in the field and the methods of analysis have correctly described a truely representative sample of the formation,

SEDIMENTATION METHOD

The Splitting of Clays

The preparation of sedimentary materials like clays is a usual preliminary for studying the clay mineralogy. Several steps are involved in the preparation of the samples depending upon the nature of claystones and clays. The clays are gently crushed with a rubber pestle to pea-sized fragments. A sample splitter, which consists of a series of inclined chutes leading alternately to two pans placed on opposite sides of the apparatus, was used. The samples were split to the desired size by resplitting the right and left halves alternately.

Coning and Quartering

This is another step towards splitting samples, to a smaller quantity. The samples were placed in a conical pile on a flat surface and separated into quarters along two diameters. The alternate quarters were retained and the others laid aside. The clay materials obtained in this way were employed for mineralogical study and in later chapters tmey will be called "whole samples".

Disaggregation of Test Samples

The term disaggregation refers to the breaking-down of aggregates into smaller clusters or into individual grains. After splitting the clay materials from the original field samples, further disaggregation is taken up depending on the nature of the materials. The use of any harsh chemicals is avoided, as these may change the nature of clay minerals. Treatment by acid and alkali may bring chemical changes and the clays may be thoroughly coagulated, which causes considerable difficulty in their dispersion.

Dispersion of Samples

The physical dispersion of 30 - 35 gms. of the test

samples in water was done in an electric drink mixer for about 20 minutes. Nearly, all the samples were dispersed without the use of electrolytes. The sample from One Tree Point, Sandy Bay, was very hard to disperse. This was boiled with water three times, centrifuged, decanted and finally dispersed with 10 cc. of sodium hexametaphosphate, (Calgon) of 10% strength, and 2 cc. of 10 N sodium hydroxide solution, for nearly 20 minutes.

The volume of suspension of the materials was made up to 1,250 ml.

Theory of Removal of clay fraction (less than 2 microns)

The fundamental principle on which the clay fraction is removed, depends on the settling of small particles with a constant velocity in water. In general, the settling velocity of the sediments depends on their radius, shape, density, surface texture and the density and viscosity of the fluid.

There is a general acceptance of uniform methods of mechanical analysis of soils and the removal of clay fractions, established by the International Society of Soil Science.

Stoke's law, connecting the velocity of sedimentation with particle size is as follows:-

$$v = \frac{2}{9} \cdot \frac{gr^2}{\eta} (D - d)$$

where,

v = velocity of sedimentation

g = acceleration due to gravity

r = radius of the spherical particles

η = coefficient of viscosity of the fluid

D = density of the spherical particles

d = density of the fluid

Under the standard conditions, the equation is expressed as -

$$v = Kr^2$$

Since both η and d depend upon the temperature, K will also depend on temperature.

Stoke's law makes various assumptions. For instance, it is assumed that all the particles behave as true sphere and they have the same specific gravity. In the international system the value of K has been defined, from the relationship connecting the particle size of clay (.002 mm.) with its settling velocity, as 34,700 at 20°C, v and r being expressed in cm. per sec. and cm. respectively. In case of temperatures other than 20°C, for the clay suspension, the time of sedimentation was corrected since, according to Stoke's law, the velocity of sedimentation is inversely proportional to the viscosity of the fluid.

Technique of removal of clay fraction

After dispersing the clay material, the volume was made up to 1,250 ml. The suspension was thoroughly stirred until the material that had collected at the bottom of the cylinder was distributed through the suspension.

A 10 cm. depth of sedimentation was taken after 8 hours of settling. This material contained particles of two and less than two microns.

A portion of this suspension was set aside for later preparation of oriented aggregates for X-ray examination and the remainder was centrifuged, decanted and dried for differential thermal analysis.

ORIENTED AGGREGATE TECHNIQUE FOR X-RAY ANALYSIS

The object of the "aggregate" technique (Nagelschmidt 1941) is to obtain better diffraction data for the basal spacing than obtained by the powder method.

In this technique of preparing the sample a clay-water suspension (as described in the last section) was allowed to settle on a glass plate placed in a horizontal position and dried slowly over sulphuric acid kept in a vacuum

desiccator. The aggregate particles were sliced with a sharp razor blade from the dried film of clay, for X-ray analysis. The thickness of the dry sediment was about 0·1 mm. and quite stable for heating to 600°C, in an electric muffle furnace, without losing its shape.

Most of the clay minerals have layer silicate structure with a marked basal cleavage and platy habit, and belong to one of the three clay mineral groups - the kaolin, mica or montmorillonite groups. The clay mineral particles settle from a deflocculated clay-water suspension on a horizontal surface and come to rest with one flake on the top of another, with the result that their basal plane surfaces are parallel. Clay specimens made from such sediments are called 'Ordered or oriented aggregates' and they act almost as single crystals, as far as the basal reflections are concerned. The basal reflections, ool, are easily recognized when preferentially oriented aggregates are employed and the mineral present is in a small proportion. These reflections, viz. 001, 002, 003 etc. give directly the thickness of the structural layers, and classify a clay mineral to a particular structural group.

However, this method has certain limitations and the technique is mostly applied to identify qualitatively various clay minerals in mixtures. In the quantitative estimation of clay minerals, it is often impossible to calculate the exact intensities of the lines, since the technique greatly enhances the basal reflections (ool) and suppresses others (hkl).

MINERALOGY OF CLAYS

INTRODUCTION

It has been established that clay is a product of the decomposition of rocks rich in aluminosilicate minerals. The decomposition may be brought about by weathering through atmospheric agencies or by hypogene processes resulting from the action of gases, vapours or solutions that originate deep in the earth's crust. Whatever the origin of clay minerals, the chief materials necessary for their formation, removed from the crustal rocks, are alumina, silica, alkali or alkaline earth elements and iron. In the case of hypogene processes these materials are transformed into clay minerals at a temperature ranging from slightly below 100°C to about 450°C in an environment that may be acid, alkaline or neutral, depending upon the pH of the invaded rocks and the acidity of the magmatic vapours. In supergene processes, the atmospheric conditions play an important role in the formation of clay minerals.

The recent extensive studies (Hendricks and Frey 1930, Kelley, Dore and Brown 1931, Grim 1942) on these different hydrated alumino-silicate minerals have proved beyond doubt, that clay materials are composed essentially of small crystalline

particles of members of one or more of a few groups of minerals known as 'clay minerals'. These minerals, which contain small amounts of alkalies and alkaline earths, are hydrous aluminium silicates, in which some of the aluminium may frequently be replaced by iron and magnesium. Although some clays are composed of a single clay mineral, most of them contain two or more. In addition to the clay minerals, clay materials may contain a variable amount of non-clay minerals, viz. quartz, feldspar, calcite, boehmite, gibbsite, goethite, pyrites and also organic matter.

By about 1930, the crystalline nature of the clay minerals and soil fractions was well established. Pauling (1930) investigated the structure of the micas and determined their layered natures. By analogy the structure of the clay minerals has been accepted as layered.

However, some work remains to be done on certain clay mineral groups and on some of the lesser known species and interstratified or mixed layer minerals. The X-ray diffraction technique has indicated the universal crystallinity of even the finest clay material (excluding organic material) so that studies involving the use of such specialised techniques as electron, microscopy, thermal analysis and chemical

analyses have determined clearly the structure and composition of clay minerals.

CLASSIFICATION, STRUCTURE, ISOMORPHOUS, REPLACEMENT and COMPOSITION OF CLAY MINERALS

Classification

There are some essential similarities of the structure of the clay minerals to those of micas, chlorites, talc, vermiculite, gibbsite etc., for they all contain alumino-silicate layers, within which there is frequent isomorphous substitution of one ion by another. This fact used in conjunction with the classification of the clay minerals, put forward by Hosking (1940), Grim (1953) and Brown (1955) has been utilised in the classification used in this investigation.

The following classification is based on the available data of structure and compositions of various clay minerals.

(a) Kandites (Kaolin minerals), dimorphic (1:1) minerals.

(b) Montmorillonites, Micas and Interstratified minerals, Pyrophyllite, talc and vermiculite, trimorphic (2:1) minerals.

(c) chlorite type minerals

(d) chain-structure type minerals, attapulgite, sepiolite and palygorshite.

(e) Amorphous, allophane group

Clay Minerals - Structure

The atomic structures of the common clay minerals have been determined in considerable detail by a number of workers and their interpretations are based on generalizations of the study of Pauling (1930).

Two structural units are involved in these layer lattices. One unit consists of an alumina or an aluminium hydroxide unit, which has two sheets of closely packed oxygens or hydroxyls between which aluminum atoms are embedded in octahedral co-ordination and in such a position that they are equidistant from six oxygens or hydroxyls. When aluminium is present, only two-thirds of the possible positions are occupied in order to balance the structure which is that of gibbsite and it has the formula $Al_2(OH)_6$. When magnesium is present, all the positions are filled to balance the structure, and it is called brucite, with the formula $Mg_3(OH)_6$. The second unit consists of a sheet of silica tetrahedra, in each of which a silicon (Si^{4+}) atom is at the centre and equidistant from four oxygen (O^{2-}) atoms or hydroxyls (OH^-). The silica tetrahedral groups are arranged to form a hexagonal network, which is repeated indefinitely to form a sheet of composition $Si_4O_6(OH)_4$.

The dimensions of these planar networks are similar and consequently composite tetrahedral - octahedral layers are readily formed. The stacking of the individual sheets can take place in any one of the following ways. A numerical ratio, such as 1:1 and 2:1 has been used for designating the kaolin and mica-type layers.

In kaolinite structure, a single tetrahedral silica sheet combines with a single octahedral one to give the unsymmetrical 1:1 dimorphic type structure. Their lattice structure does not expand with varying water content, because of the attraction of O and (OH) layers which are adjacent when kaolinite units are stacked one above the other.

In the second type a singly octahedral sheet combines with two tetrahedral sheets, one on each side of the octahedral sheet, to give the symmetrical 2:1 trimorphic type structure of pyrophyllite, talc and the micas. It may be explained that in the trimorphic type structure there have been included talc and pyrophyllite, the clay micas (illites etc.) and the swelling minerals (montmorillonoids, vermiculite), in view of the very close inter-relations of these minerals.

These dimorphic and trimorphic structures determine

the grouping of the clay minerals and they are further subdivided into dioctahedral and trioctahedral series, depending on whether two thirds of them are filled with trivalent ions (as in gibbsite layer) or all the possible positions filled in the octahedral sheet with divalent ions (as in brucite sheet). The mineral brucite, has a similar structure to gibbsite except that all the possible positions are occupied by magnesium.

In the mixed-layer minerals, layers of two or more minerals alternate in the same crystallite. Mixed-layer structures are of two different types, one type is where there is regular interstratification of layer clay minerals, and the other type is where the clay minerals are randomly interstratified.

In the chlorites the structure consists of alternate mica-like and brucite-like layers and they consist of two tetrahedral and two octahedral sheets.

The chain structure type clay minerals resemble the amphiboles in their structural characteristics.

The allophane minerals are amorphous to X-ray diffraction (Ross and Kerr 1934).

Isomorphous Replacements of Ions within the Crystal Lattices of the Clay Minerals

The crystal structures necessarily form the basis of the classification of clay minerals, although changes in chemical composition, as affected by the substitution of one ion by another is common. These substitution depend more upon ionic size than upon valency or chemical similarities. The electrical neutrality may be upset within the sheets by the replacement of one ion by another of different valency. The simplest case of such replacement is, when the ions are equal both in charge and size, and this accounts for the ready interchangeability of Mg^{++} and Fe^{++} in so many minerals. In muscovite, the potassium (K^{+}) can be replaced to a limited extent by the slightly smaller sodium (Na^{+}) ion to give paragonite, but not by the much smaller lithium (Li^{+}). Lithium, however, can readily replace the smaller sized aluminium (Al^{+++}) ion in octahedral co-ordination, to give the large group of lithia-micas. Aluminium ion, in addition, may be commonly replaced by Fe^{+++}, Fe^{++}, Mg^{++}, Mn^{++} and Ti^{+++}, all of which are similar in size. Si^{++++} (silicon) ion is frequently replaced by Al^{+++}, in the tetrahedral co-ordination, and sometimes by Fe^{+++} and Cr^{+++} (chromium).

There is a limit to the extent to which such substitution can take place, for an alternative type of structure becomes more stable when the limits of composition are overstepped. However, electrical neutrality must be maintained when there is substitution by ions of lower valency, e.g. when Si^{++++} is replaced by Al^{+++}, or Al^{+++} by Mg^{++}, the replacing ion of a lower valency must be accompanied by other cations to restore neutrality.

Kaolin Minerals

In the kaolin group of minerals and pyrophyllite there is little isomorphous replacement of ions. Therefore, the layers are practically neutral and there is no substitution by other cations to restore neutrality in the lattice. Similarly, when in pyrophyllite $2Al^{+++}$ are replaced by $3\ Mg^{++}$ to form talc, there is little additional of any external ions to maintain the neutrality. However when Si^{++++} of the pyrophyllite or talc is substituted by Al^{+++} to form muscovite or biotite respectively, the layers produced are electrically negative and must be neutralized by the additional of K^{+} ions.

Montmorillonite Minerals

In the montmorillonite minerals having the theoretical formula $(Al_{3\cdot33}\ Mg_{0\cdot67})\ (Si_8)\ O_{20}\ (OH)_4$ for the

$$M^{+}_{0\cdot67}$$

end member, the silicate-layer charge is due entirely to the replacement of Al^{+++} by Mg^{++} in the octahedral sheet. In addition most montmorillonite specimens have some replacement of Si^{++++} by Al^{+++} in the tetrahedral sheet, and of Al^{+++} by Fe^{+++} in the octahedral sheet, so that there is necessarily an extensive replacement in both these sheets and the extra cations H^{+}, Na^{+}, K^{+}, Ca^{++}, Mg^{++} etc. are required to restore neutrality. These extra cations lie rather loosely between the layers and are thus readily exchangeable. The phenomenon of base exchange results partly from this type of replacements and the montmorillonite minerals can be named after their predominant exchangeable cations between the silicate layers.

Composition of Clay Minerals

The Kaolin Minerals (Kandites)

The minerals recognised as comprising the kaolin group

are nacrite, dickite, kaolinite, metahalloysite, halloysite and anauxite, having a relatively simple layer structure formed by the union of a tetrahedral silica sheet and one octahedral sheet of the gibbsite type. The kaolin layer is about 7·2 Å thick. Since the ion present in the octahedral sheet is predominantly Al^{+++}, the minerals of the kaolin group are all of the dioctahedral type.

The chemical formula, $Al_2Si_5O_5(OH)_4$ basically covers all members of the group except halloysite and anauxite. Halloysite having the chemical formula $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$, contains two extra molecules of water, which can be removed by heating to below 200°C. Anauxite contains excess silica and has a $SiO_2:Al_2O_3$ ratio varying from 2:1, of the normal kaolin minerals, to a maximum of 3:1. Despite changes in silica and alumina ratio from 2:1 to 3:1, anauxite gives X-ray patterns very similar to that for kaolinite.

The Mica Minerals (Muscovite, Biotite, and the clay micas - illites).

The micas are silicates of the three layer (2:1) type (trimorphic) minerals with a non-expanding lattice, and on their X-ray patterns they show a series of (ool) lines that

includes one at about 10Å. Micas may be divided into two general categories:

(a) true micas, appearing mainly as well developed crystals during magmatic differentiation of igneous rocks and pegmatites. True micas of dioctahedral and trioctahedral types occur with replacements common in both.

(b) clay micas, formed generally under weathering conditions of lower temperatures as components of sedimentary rocks and distinguished from 'true micas' by their smaller crystal size, higher content of silica and water and lower content of interlayer potassium.

In the case of clay micas a division is possible depending on their physical, chemical and mineralogical properties. Recently Walker (1950) has recognised trioctahedral clay micas in soils, which enables the division into dioctahedral and trioctahedral series. Despite this similarity with the true micas, the clay micas differ from the true micas in many respects for the particle size of the clay mica is smaller than that of true micas and potassium content is lower with a corresponding increase in hydration or water content. Despite the fact that the trioctahedral truemicas (biotite) are the more common of the true micas in igneous rocks

(Clarke 1924) the dioctahedral clay micas are the more common constituents of the clay materials. A classification of the clay micas on the basis of decreasing potassium content (K^+) and increasing hydration has been suggested by Grim, Bradley and Brown (1951) who have shown a progressive alteration of the micas through various intermediate (hydromuscovite, illite etc.) to montmorillonites and vermiculites.

The Montmorillonite Minerals (Smectites)

The smectites are generally extremely fine grained clay minerals. Although variable in composition, all the members give similar X-ray diffraction patterns and are therefore of the same structural type. The minerals are formed of compound layers, composed of a gibbsite $Al(OH)_3$ layer between two silica (SiO_4) layers. The chemically combined water content is less than that in kaolinite, because each gibbsite layer is bonded to two silica layers instead of one and thus more of its hydroxl ions are replaced by oxygen ions for interlayer bonding purposes. The smectites all have an expanding lattice and a high cation exchange capacity. They are divided on chemical data into the dioctahedral and trioctahedral series depending upon whether two-thirds or all

the octahedral positions are occupied. Considerable variation occurs as a result of isomorphous replacements in both tetrahedral and octahedral layers and therefore various species are distinguished according to their composition.

Dioctahedral Smectites

The most abundant dioctahedral smectite is montmorillonite. The theoretical end member

$$(Al_{3.33}\ Mg_{0.67})\ (Si_8)\ O_{20}\ (OH)_4$$

$$M^{+}_{0.67}$$

shows the silicate layer charge to be due entirely to replacement of Al^{+++} by Mg^{++} in the octahedral sheet. Most montmorillonites have in addition some replacement of Si^{++++} by Al^{+++} in the tetrahedral sheet and of Al^{+++} by Fe^{+++} in the octahedral sheet.

Beidellite is an Al- smectite which contains no Mg^{++} or Fe in the octahedral sheet, the silicate-layer charge being derived from replacement of Si^{++++} by Al^{+++}. The structure formula is

$$M^{+}_{0.67} \cdot Al_4\ (Si_{7.33}\ Al_{0.67})\ O_{20}\ (OH)_4$$

Nontronite

This is an iron beidellite type mineral with practically all the Al^{+++} replaced by Fe^{+++}, giving a theoretical formula:

$$M^{+}_{0.67} \cdot (Fe^{3+}_{4}) \ (Si_{7.33} \ Al_{0.67}) \ O_{20} \ (OH)_{4}$$

Trioctahedral Smectites

Saponite (Mg rich), sauconite (Zinc analogue of saponite), hectorite (saponite mineral with Li^{+}) etc. are the recognised varieties of the trioctahedral smectites.

METHODS OF IDENTIFYING CLAY MINERALS

Clays and soils have been studied in some way or another for a long time. But their study proved particularly difficult because they may be extremely fine grained and very complex mixtures. The petrographic method has been of little use because of the very small size of the particles of clay minerals. About 30 years ago modern analytical research tools, particularly X-ray diffraction became available and, for the first time, precise determination of the identity and character of the constituents of the clay materials was made. In the early nineteen twenties, additional analytical tools, such as differential thermal analysis and electron microscopy, had been developed and used for clay mineral analysis.

Clay mineralogy includes work in many different fields; chemistry, physics, mineralogy and geology.

There are several methods of studying clay minerals and they are as follows:-

CHEMICAL ANALYSIS

This is a very lengthy procedure. However it is

used as a supplement to other methods for distinguishing between the broad groups of clay minerals and may be extremely valuable in determining the nature of isomorphism. In this method the SiO_2:Al_2O_3 ratio is determined by analysis and is used to distinguish between the two-layer clay minerals (kaolinite) and the three-layer clay minerals (montmorillonites and clay micas). But this ratio is of only limited value in determining which particular clay mineral is present in a clay material under investigation. The same ratio is characteristic of all the members of the kaolin group; kaolinite, dickite, nacrite and halloysite. In the case of smectites, there is rather a wide variation in the SiO_2 : Al_2O_3 ratio because they form an isomorphous series.

It would be quite logical to conclude that the SiO_2 : Al_2O_3 ratio or the SiO_2 : (Al_2O_3 + Fe_2O_3 + MgO) ratio cannot be used safely for identifying clay mineral species. Nevertheless, the chemical analysis method is quite essential and useful in determining the nature of isomorphism in montmorillonites.

Iron determinations were made of a few selected samples (3, 10, 16 and 19) rich in montmorillonite, in order

to confirm nontronite.

2. PETROGRAPHIC METHOD

Grim (1953) contends that the petrographic method is of use in clay mineral analysis. However, the claim was not supported in the present investigation and the failure of the method was believed to be due to the very fine-grained character of the clays investigated.

3. DYE ADSORPTION METHOD

Dyestuffs and other organic materials have been employed in clay mineral identification. The reaction and colour change is believed to result from an acid-base type of reaction in which the natural or acid-treated clays react as acids or an oxidation-reduction reaction mechanism, in which certain ions, mainly ferric, contained in the crystal lattice of the clays, effect an oxidation of the substance. The substances bringing about colour change by acid - base type of reaction are triphenylmethane, azine and azo dyes and by the oxidation-reduction reaction are benzidine and other aromatic amines (Hendricks and Alexander (1940) and Hauser and Leggett (1940).)

Such staining techniques are often employed to identify rapidly the clays and soils but the method is not much encouraged, as the results may be extremely variable because of impurities and complex mineralogical associations. Manganese dioxide, as an impurity, in the clay may cause the oxidation-reduction reaction with benzidine even in the absence of adsorptive clays, and the presence of ferrous iron or any other reducing agent may inhibit the colour forming reaction.

The author's attempt to carry out clay-stain tests on the samples under investigation was quite unsuccessful because of the complex mixture of the clay minerals, interlayerad lattices of some clay minerals and presence of traces or organic matter.

4. ELECTRON MICROSCOPY METHOD

The electron microscope studies have revealed the morphological characteristics of the clay minerals and their shape and size have been studied. The method of electron microscopy is perhaps the most reliable, e.g. two clays may give the same X-ray pattern and differential thermal curve but they may look quite different.

5. DETERMINATION OF CATION - EXCHANGE CAPACITY

The property of base-exchange of clays is like that of zeolites and permutites which exchange their bases for others and are used for softening of water. The base-exchange capacity is measured in terms of milli-equivalents per gram or per 100 grams. Grim (1939) has determined the base-exchange capacity of the clay minerals and found that montmorillonite has the maximum of 70 to 120 milli-equivalents per 100 grams fro readily exchangeable cations, while kaolinite has the least.

This method has its own limitations as there is no single capacity value which is characteristic of a given group of clay minerals.

6. DIFFERENTIAL THERMAL ANALYSIS METHOD

A. Introduction

The differantial thermal method of analysis is employed in the mineralogical investigation of clays and other minerals, which upon heating undergo endothermic or exothermic reaction at characteristic temperatures. The principle of the method was first suggested by Le Chatelier (1887). It was

not until the late 1930's that the method began to be used for semiquantitative study of clay minerals. The method is not only limited to clay mineral study ~~set~~ but may be applied also to an amorphous material, provided it undergoes a thermal reaction (endothermic and exothermic change). Since 1930, further development in the technique began with the work of Orcel (1935), Orcel and Caillere (1933) and Insley and Ewell (1935). Norton (1939) published an improved design of furnaces, sample holders and photographic recording equipment for differential thermal apparatus, which formed the basis for several units by Grim and Rowland (1942), Berkelhamer and Speil (1945) etc.

B. Method and Theory of D.T.A.

In differential thermal analysis a sample of the material under investigation and a thermally inert substance such as calcined alumina placed side by side in a suitable sample holder, are heated in a furnace to about 1,000°C. In this technique a dual-terminal thermocouple is used, one junction is inserted in the inert substance (thermally inert within a given temperature range), while the other junction is placed in the sample. The inert substance and the sample

are heated simultaneously at a constant rate. The differantial thermocouple gives an output only when the sample becomes hotter or cooler than the inert material, i.e. when a thermal reaction takes place in the sample. The output is measured and recorded as a plot of temperature difference versus furnace temperature. In the 'differantial thermal curve' certain endothermic and exothermic reactions are shown by the peaks below and above the base line respectively. In fact these differential curves are not the true curves, but curves for temperature difference against temperature. However, the nature of the peaks, their intensities and the particular temperatures at which they occur are quite characteristic for a clay mineral or any other hydrous mineral.

The theory of differential thermal analysis for quantitative estimation of the components has been discussed by Speil (1944), Kerr and Kulp (1948) and Jefferies (1944). It is established that the area of a peak is directly proportional to the mass of the reacting substance (sample). Carthew (1955) determined that with decrease in particle size the peak becomes narrower and asymmetric, and there is reduction in temperature of the main dehydroxylation peak but

no significant change in the peak area. Attempts were made to use the D.T.A. method for quantitative determination of components present in a sample.

C. Limitations in Differential Thermal Analysis

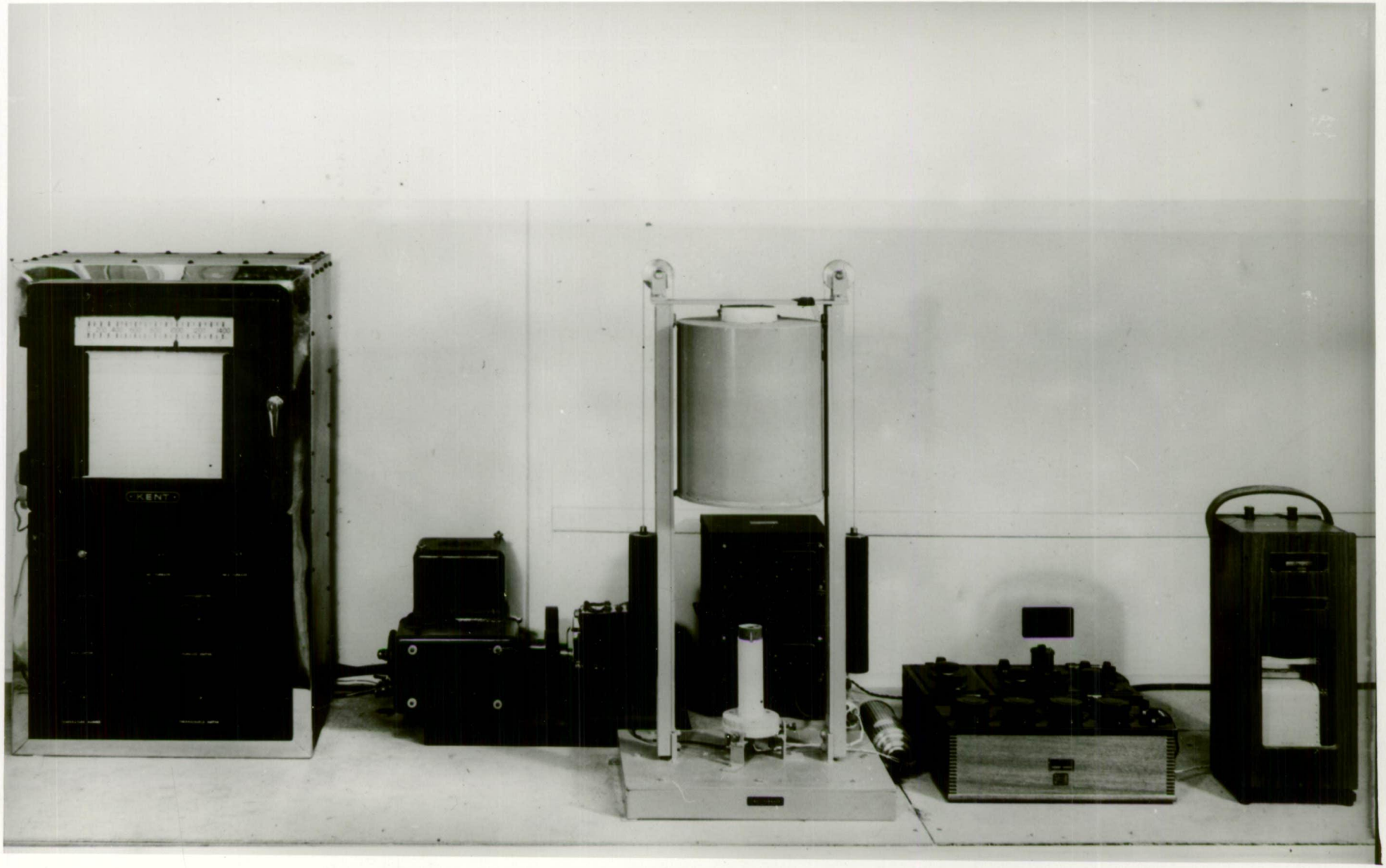
The differential thermal method of analysis was used in correlating the results obtained by the X-ray examination. Since the area of a peak is proportional to the mass of the reacting substance or the amount of heat involved in a reaction (Speil 1944, and Kerr and Kulp 1948), the differential thermal curves provided useful quantitative data of the mineral composition of the clay samples. This type of empirical relation was fairly accurate in the quantitative estimation of kaolinites of comparable crystallinity, but for micas and montmorillonite minerals, the limitations were considerable. Another limitation and source of error in both qualitative and quantitative determination by the differential thermal method of analysis was the near occurrence of the overlapping endothermic and exothermic peaks, therefore the method could not be used confidently to identify montmorillonite in the clays.

D. Usefulness of the Method

Among the many methods of studying clay minerals (discussed earlier) the differential thermal method is very useful to supplement the results obtained by X-ray examination. Although it was early realized that the method was not fully developed as a diagnostic technique for clay - mineralogical investigations, it nevertheless gives a considerable amount of information and is becoming popular because of its simplicity and quick determination (about $1\frac{1}{2}$ hours). No doubt, the method has certain limitations, for quantitative analysis work (Mackenzie 1957). But in this investigation the writer has experienced certain advantages in the differential thermal method. For instance, the presence of an abnormal montmorillonite (to be fully discussed later) was detected rapidly by this method giving an endothermic peak about 550°C, (while a normal montmorillonite has its main endothermic peak at 700°C). X-ray data indicated that the mineral was a normal momtmorillonite, with distinct lattice expansion characteristic of the mineral. The main point of interest lies in the thermal characteristics of the mineral, which so far as can be ascertained are quite different from those of normal smectite. A similar example of an anomalous illite has been described by Mackenzie, Walker

DIFFERENTIAL THERMAL ANALYSIS APPARATUS

PLATE IA



and Hart (1949), in which the endothermic peak occurs at about 700°C, while a normal illite has its endothermic peak at 550°C although the mineral had similar X-ray and chemcial data to a normal illite. These peculiarities in the behaviour of clays can be shown only be a differential thermal method and when used in conjunction with other methods particularly X-ray diffraction, it gives a valuable clue in detecting the mineral entities and clay mineral structures. Besides, the method is quite useful in detecting and estimating small amounts (even less than 1 per cent) of gibbsite, goethite and calcite, the kaolin group of minerals can be reasonably determined to the nearest 5 per cent.

E. Equipment Used

The differential thermal analysis equipment used in this work is that of the Mineralogical laboratory of the Division of Building Research, Commonwealth Scientific and Industrial Research Organization, Highett, Victoria. This equipment has been developed in their laboratories for use in the mineralogical investigation of clays and is described by Carthew and Cole (1953). The apparatus is shown in Plate 14 and described briefly as follows.

A vertically mounted furnace, externally wound, of electricl resistance type was used. The sample block is constructed from heat-resistant steel (chromium-tungsten) which does not scale and deform. Both of them were heated to 1000°C at a constant heating rate of 10°C per minute. The furnace temperature was recorded and controlled with a Kenty type - 7 gear box and a type 100 - R adjustable transformer. The furnace temperature was recorded as the temperature of the inert material, with a platinum/13 per cent, rhodium-platinum thermocouple. The differential temperature was measured with a platinum 10 per cent rhodium-platinum differential thermocouple. The output from the differential thermocouple was amplified by a Tinsley galvanometer-type D.C. amplifier and recorded by an Evershed and Vignoles recording ammeter. The sensitivity employed was such that the full chart width corresponded to an output of the differential thermocouple of 200 microvolts.

F. Analytical Procedure and Sample Preparation

For determining the differential thermal curves of the whole samples and their clay fractions (less than 2 microns) the materials were ground to pass 70 mesh. About 0·8 gram of sample was used in each run and mixed with about 0·5 gram of calcined alumina (for dilution). The function of a diluting

material has been considered by Grimshaw and Roberts (1953) and Sabatier (1954), where a better correlation between peak area and amount of reactant is obtained, and specimen shrinkage is minimized.

The intimate mixture of the sample and inert material (diluent) was packed into the sample holder by tamping first with a rod and finally with the finger tip. The same packing procedure was always followed for all the samples for reproducibility in the results. Calcined alumina was used as a thermally inert material. After the analysis the sample was allowed to cool and removed by suction with a vacuum cleaner.

7. X-RAY DIFFRACTION METHOD OF ANALYSIS

A. Introduction

Of all the methods used for mineral identifications, X-ray diffraction is undoubtedly the most valuable single method for clay mineralogical investigations and is of great importance for studying their crystalline nature. It was first used by Hendricks and Fry (1931) and Kelley et ab. (1931) and later by other workers for mineral identifications of soil colloids and clay materials.

B. Principle of Method

The principle of the method is simple and X-ray beam is diffracted by a crystal. Bragg (1933) has proved that if an X-ray beam of wave length λ is incident at an angle θ on a set of uniformly spaced atomic planes a distance d apart, then a reflected X-ray wave of maximum intensity could only occur if $n\lambda = 2d \sin\theta$, where n is a whole number. This equation is known as Bragg's Law and from it, it is possible to find out λ, if d and θ are known, or the interplanar spacing 'd' can be calculated, if λ, the X-ray wave length, is known and θ, the angle of reflection or the Bragg angle can be measured from the X-ray photograph.

C. Methods and Technique

The two methods of diffraction used in this investigation are the powder and aggregate techniques.

1. Powder Method

For the powder patterns the whole sample crushed to pass 200 mesh was mounted in a wedge and kept oscillating. A series of X-ray beams in form of cones are reflected from the

disoriented crystals and they formed arcs of circles on a strip of photographic film placed in the form of a cylinder around the sample. In this way each mineral gives a set of reflections which are characterised by their position on the film, width and relative intensity, and the X-ray powder pattern of a mixture of clay minerals is superimposed on the same film. By the use of standard photographs of minerals or the A. S. T. M. card index, the crystalline constituents of a mixture can be identified.

Limitations in X-ray Examination

It may also be mentioned that the powder method has some limitations, e.g. small percentage of unknown substance may remain unidentified because the reflections may be too weak to be observed, and the percentage of minerals that can be identified varies, as some of them give very sharp and strong reflection (1% quartz) as compared to others which produce relatively faint and weak reflections (clay minerals). Despite these limitations, attempts were made to estimate quantitatively the different minerals present in the clays, based on the visual examination of the itensities of the diffraction lines. The results of analyses were also compared to the X-ray photographs of simple mixtures prepared by the Mineralogical laboratory.

(C.S.I.R.O.), although difficulties again arose due to the differantial absorption effects (Brindley 1945) when one mineral is more crystalline than the other and preferential orientation of the clay minerals.

II Aggregate Technique

In the aggregate technique (Nagelschmidt 1946) the ordered aggregates were prepared form a less than 2 microns suspension (as discussed on Page 24) of clays and examined by the X-ray diffraction method. In this technique the clay particles are largely oriented with their basal planes parallel to the plane of sedimentation. The basal reflections measure the height of unit cell of the layer lattice silicate minerals and were recorded with greater intensity and more clearly than on X-ray powder patterns. These enhanced basal spacings (oo1) on X-ray photographs are the best criterion for differentiating between various clay mineral groups, particularly when a mineral is present in a small quantity in a mixture with a small grain-size. However these are again limitations in the quantitative estimation of minerals by this method and these have been already discussed.

D. Cameras Used

A modified X-ray camera of 3·0 cm. radius, capable of recording spacing of the order of 20 Å was used for all the clay samples. But for two of them (20 and 22) a larger camera of 5·73 cm. radius was used in order to establish the presence of higher spacings. In these analyses monochromatic X-rays were allowed to fall upon the powder and aggregate sample and the diffracted rays were recorded on a photographic film Copper $K\alpha$ radiations were used, while white and $K\alpha$ radiations were removed by means of a nickel filter.

Six X-ray diffraction patterns were obtained for each clay aample, as follows:

1. Randomly oriented powder
2. Randomly oriented powder treated with glycerol
3. Randomly oriented powder heated to 600°C
4. Untreated oriented aggregate
5. Oriented aggregate treated with glycerol
6. Oriented aggregate heated to 600°C

E. Measurement of lines in Patterns and Conversion to d Values

After taking the X-ray photographs, the first step in their interpretation was a careful measurement of the positian

of lines and bands and a visual estimate of their intensities as V.V.S. to V.V.W. (very very strong to very very weak) These distances (25) in cm. were converted to angular measure and then to their interplanar (d) spacings from the tables (Bragg 1944). Film shrinkage was also taken into account.

About 50 per cent of the X-ray photographs were measured and interpreted and the interpretation of the remainder were based on comparison with the former.

F. Effect of Organic Compounds (Glycerol, Glycol) and their Use in Clay Mineral Identification

Bradley (1945) and MacEwan (1944, 46) have shown that the non-ionic polar ogranic molecules could be absorbed by the clay minerals, particularly montmorillonite and halloysite. The organic ions are held around their edges, enter the interlayer space and replace the water. The layers of glycerol - montmorillonite complex are, therefore, more uniformly spaced than hydrated montmorillonites and a clearer succession of higher order is obtained.

It is doubtful if montmorillonites can be identified in the presence of chlorite and vermiculite on the basis of

interplanar spacings alone since all three minerals give the same line (at 14 Å) in an X-ray pattern. Therefore the method (Bradley 1945 and MacEwan 1944 and 1946) of forming glycerol-montmorillonite complex was utilized and applied to all the whole samples as well as to oriented aggregates, to distinguish montmorillonite from chlorite and vermiculite. The method gave an enhanced first order (001) basal reflection at 17 - 18 Å which was distincly separate from and clearer than any other line likely to arise from other minerals.

The sensitivity of the method was observed, when relatively smaller proportions (less than 5%) of montmorillonite could be detected in mixture of other minerals (Kandites, micas, chlorites etc.) and it was found much easier to distinguish montmorillonite from chlorite and vermiculite, which did not show a similar increase in the interlayer spacing when treated with the organic liquid (glycerol).

G. Effect of Heat Treatment and its use in Clay Mineral Identification

The X-ray identification of minerals for a detailed analysis of a complex mixture of three, four or more minerals is often facilitated by heat treatment (500° - 600°C). For example,

if kaolinite is present in a mixture of other clay minerals, the latter may remain unidentified due to the many reflections from the kaolinite. However, if the clay material is heated to about 600°C for an hour the kaolinite lattice breaks down to a non-crystalline state, therefore its reflections are eliminated.

Another advantage in the heat treatment as determined was the identification of the chloritic clay minerals when in association with kaolin minerals. A chloritic mineral may be confused with a kaolin mineral, when the X-ray pattern does not show its characteristic 14 Å reflection, since the second and fourth order reflection at about 7·0 Å and 3·5 Å are very close to the corresponding spacing of the kaolin minerals. A heat treatment (600°C) was always made in all the samples in order to convert kaolin minerals to an amorphous state, whereas chlorite at this temperature is only partially dehydrated resulting in increased intensity of the 14 Å reflection.

Similarly a swelling type of chlorite (Stephen and MacEwan 1949) may be confused with montmorillonite. But the distinction can be made by heating the clay sample to 500°C. The chlorite will give a strong 14 Å line, whereas montmorillonite gives a reflection at 10 Å.

TEST FOR DISTINGUISHING BETWEEN MONTMORILLONITE AND NONTRONITE

Due to the presence of a lower dehydroxylation peak at about 550°C in the differential thermal curves the clays were suspected to be characterised by nontronite, therefore it was necessary to carry out the 'Greene - Kelley test' (1952, 53). This test is very useful in differentiating between montmorillonite and other members of the montmorillonoids (e.g. nontronite). The test was carried out on a few selected clay samples (1, 1A, 2, 5, 10, 11, 16, 19, 24, 26) having abnormal montmorillonite as their major constituent.

The test and its principle is described as follows: The principle of the method is that montmorillonite saturated with small ions, for example lithium, is difficult to rehydrate after being heated at moderate temperatures (200°C). This behaviour of lithium ions is confined to montmorillonite only and forms the basis of the 'Greene - Kelley test' which enables the mineral to be easily distinguished from other members of montmorillonoids.

The test can be satisfactorily applied to the oriented aggregate flakes or powders. The portion of clay suspension (less than 2 microns fraction) was treated 3-4 times with 3N lithium chloride, centrifuged and decanted. The excess salt

(lithium chloride) was removed about three times with warm 80 per cent ethyl alcohol. The oriented aggregates prepared in the same manner and described in the chapter on "Preparation of Sample" were heated to 200°C for approximately 15 hours and used for X-ray examination

Observations and Conclusions

The clay samples containing abnormal montmorillonite showed no rehydration or irreversible collapse of the 10 Å line, thus proving a strong presence of an abnormal montmorillonite in the clays.

It can be concluded therefore, that the lower dehydroxylation peak in the differential thermal curves cannot be attributed to the mineral nontronite. Further, the absence of nontronite was confirmed by chemical analysis done on four selected samples (3, 10, 16 and 19). The percentages of Fe_2O_3 determination are 9·59, 7·46, 10·91 and 2·37 respectively. Since these Fe_2O_3 percentages are very low as compared to nontronite (20 per cent Fe_2O_3), the latter was certainly not a constituent of the clays.

STANDARD X-ray DIFFRACTION DATA FOR IDENTIFYING MINERALS COMMONLY OCCURRING IN CLAY MATERIALS

For determining the minerals present in the clay materials and interpreting their powder diagrams (random orientation) and the oriented aggregates (basal reflections), the results (given in a forthcoming chapter) were compared with corresponding data for standard minerals. The X-ray diffraction data can also be found in the "American Society for Testing Materials Card Index" (1950). In this publication the data is classified in order of the strongest reflections. It includes a wide range of substances among which a large number of clay and other minerals are also found.

The X-ray data in the accompanying table (Table I) is summarised from the literature on clay minerals (Kerr 1950 and Brindley 1951) and was used for quick interpretation of the X-ray photographs of the clay samples studied. Their interplanar spacings (d) are arranged in order of the most important of the strongest lines commonly met in these clay materials.

TABLE I.

X-ray Data.

(RANDOM ORIENTATION)

STRONGEST LINES

KAOLIN GROUP		MONTMORILLONITE		MONTMORILLONITE GLYCEROL		MICA GROUP		VERMICULITE		CHLORITE		QUARTZ		FELDSPAR GROUP		GIBBSITE		GOETHITE		HAEMATITE		CALCITE		SODIUM CHLORIDE	
d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I
7.15	vs	14-15	vs	17.7	vs	10.0	s	14.0	vs	14.0	5-10	4.21	7	4.0-4.2	ms-s	4.83	10	4.15	10	2.69	10	3.03	vs	2.82	10
3.57	vs	4.42	s	4.42	s	5.0	s	4.58	mw	7.0	8-10	3.35	10	3.7	ms-s	4.34	6	2.67	6	2.51	8	1.92	vs	1.90	5
2.33	s	2.55	s	2.55	s	4.50	s	3.51	m	4.7	7-9	1.81	8	3.2	vs	2.45	5	2.43	7	1.69	8	1.87	s	1.6	2
						3.33	vs	2.63	mw	3.5	10	1.54	6			3.37	5	1.71	6						
						2.57	s																		

BASAL SPACINGS IN

PREFERENTIALLY ORIENTED AGGREGATES.

KAOLINITE			HALLOYSITE			MONTMORILLONITE	MONTMORILLONITE + GLYCEROL			MICA GROUP			VERMICULITE			CHLORITE		
ool	d	I	ool	d	I	Basal Spacings	ool	d	I	ool	d	I	ool	d	I	ool	d	I
(001)	7.14	vs	(001)	10.0	-	DEPENDS ON (001) which varies with the nature	(001)	17.7	vs	(001)	10.0	s	(001)	14.0	vs	(001)	14.0	vs/m
(002)	3.57	vs				of interlamellar exchangeable cations. On	(002)	8.85	s	(002)	5.0	ms	(002)	7.0	m	(002)	7.0	vs/s
(003)	2.37	s				heating to 500°C, the basal reflections are	(003)	5.9	m	(003)	3.33	vs	(003)	-		(003)	4.7	vs/w
(004)	1.78	m				very similar to micas, talc and pyrophyllite.	(004)	4.40	ms	(004)	2.50	mw	(004)	3.50	m	(004)	3.5	vs
							(005)	3.54	ms									

Index to Abbreviations: d = spacings in Å; I = intensity; vs = very strong; s = strong; m = medium; mw = medium weak; ms = medium strong.

RESULTS OF INVESTIGATION OF MINERALOGICAL COMPOSITION OF THE CLAYS

INTRODUCTION

Quantitative estimates of the mineral composition of the clays have been largely based critically on the accuracy of the methods (X-ray diffraction techniques and differential thermal analysis) followed. Although estimation of the percentages of clay and non-clay minerals has been attempted in this thesis, the author fully recognizes the difficulties encountered in such an attempt. Such difficulties and the limitations of the methods used have been fully discussed in a previous chapter.

However, despite the limitations, the writer feels that the quantitative data of the mineral composition given in this thesis is reasonably accurate, at least for comparing the relatives proportions of one clay sample with another.

CLAY FROM GLENORA (SAMPLE No. 1).

Table 2 - X-ray diffraction measurements data
(Ni filtered, copper Kα radiation)

Whole Sample (Wedge-powder) (film recorded)					
Untreated		Treated with glycerol		Heated to 600°C	
I	d	I	d	I	d
vs	15·08	vs(di)	18·19	m(diff)	10·1
vw	7·36	vvw	9·92	m	4·47
m	4·47	vvw	8·93	m(sp.)	4·27
m	4·27	vw	7·38	vvw(sp.)	4·08
vvw	3·75	m	4·50	vw(sp.)	3·75
vs	3·35	m(sp.)	4·26	vvw	3·45
vvw	3·24	vvw(sp.)	4·07	vs(sp.)	3·35
w	2·56	vvw(sp.)	3·72	vvw(sp.)	3·23
vw	2·46	vvw(br.)	3·55	vvw(sp.)	2·94
w	2·37	vs(sp.)	3·37	w	2·58
vvw	2·29	vvw(sp.)	3·23	w(sp.)	2·45
vvw	2·22	vvw(br.)	2·94	w	2·28
vw	2·13	w(dif.)	2·56	vvw	2·25
vw	1·97	w(sp.)	2·47	w	2·12
w	1·81	vw(sp.)	2·36	w(sp.)	1·97
vw	1·66	w(sp.)	2·27	m	1·81
m	1·54	vvw	2·24	w	1·66
vw	1·49	w(sp.)	2·11	w	1·54
vvw	1·45	w	1·97	m	1·37
m	1·37	m(sp.)	1·82	w	1·28
vw	1·28	w	1·66		
vvw	1·25	m	1·54		
		m	1·49		
		w	1·45		
vvw	1·22	vs(sp.)	1·37		

CLAY FROM GLENORA (SAMPLE No. 1)

Table 2 - continued

Oriented Aggregates (film recorded)					
Untreated		Treated with glycerol		Heated to 600°C	
I	d	I	d	I	d
vw(di)	18.01	vs(di)	18.22	m	10.01
vw	10.12	w(di)	9.90	m(di)	4.98
s	7.12	m	7.21	vw	4.46
vvw	4,94	vvw	5.03	m	4.25
w	4.44	vw	4.43	vvw	3.78
m	4.21	m	4.23	vvw	3.52
s	3.57	m(di)	3.55	vs	3.33
vs	3.31	vvs	3.32	vvw	3.24
vvw	2.57	vvw	3.24	vvw	2.57
vvw	2.46	vvw	2.93	vw	2.46
vvw	2.38	w	2.56	vw	2.30
vw	2.12	w	2.43	vw	2.13
vw	1.99	vvw(di)	2.36	vw	1.99
w	1.80	vw	2.24	w	1.82
vw(br)	1.67	w	2.1	vw(di)	1.67
vw	1.54	w	1.98	w	1.55
vw	1.47	m	1.87	w	1.37
vw	1.37	w(di)	1.67		
		w	1.54		
		w(di)	1.49		
		w	1.37		

Key to abbreviations used:

vvs = very very strong

vs = very strong

s = strong

ms = medium strong

m = medium

mw = medium weak

w = weak

vw = very weak

vvw = very very weak

sp = spotted

br = broad

di = diffuse

MINERALS IDENTIFIED

The following minerals in order of abundance were identified from the X-ray diffraction patterns of clay sample (no. 1) from Glenora.

Montmorillonite (or montmorillonoid - MacEwan 1951) the dominant clay mineral was identified by the presence of a very strong line at 15·08 Å, which expanded with glycerol treatment to 18·19 Å and collapsed to a spacing of 10·1 A, on heating the clay to 600°C.

Among the non-clay minerals, quartz was abundant. It was characterised by a very strong line at 3·35 Å and a medium line at 4·27 Å. A very weak reflection at 3·75 Å in the powder pattern was due to feldspar which was present in traces only.

The clay group was identified in the X-ray diffraction pattern (oriented aggregate) by its prominent basal reflections at 7·12 Å (001) and 3·57 Å (002) respectively. Since the 7·12 Å and the 3·57 Å reflections were oriented lines, the particular mineral in this group was kaolinite. On heating the clay to 600°C, the mineral (kaolinite) decomposed to a non-crystalline state with a sharpening of the basal reflections due to illite

(term used hereinafter Grim, Bray, and Bradley, 1937, for mica-like group of clay minerals and anhydrons montmorillonite)

An illitic mineral, present in small amount, was identified on the basis of a characteristic reflection at 10·12 Å with a weak intensity (diffuse) which remained unexpanded following treatment with glycerol. The only analytical data for an illite is that it is a non-expanding 10 Å mineral.

QUANTITATIVE ESTIMATION OF MINERALS FROM X-ray PATTERNS

For a quantitative estimate of the minerals present in the clay (1) from Glenora (based chiefly on X-ray examination), the reflections were compared with suitable reflections from the standard binary mixtures of known proportions of montmorillonite and quartz and kaolinite and quartz. The intensity ratios indicated a mixture of montmorillonite 40 per cent, quartz 30 per cent and kaolinite 20 per cent with small amounts of illite 5-10 per cent and traces (less than 5 per cent) of feldspar. The clay fraction (less than 2microns) contained an increased proportion of clay minerals and a relative decrease in its quartz content. Its mineral composition was montmorillonite 50 per cent, kaolinite 25 per cent, quartz 10-15 per cent and mica 5-10 per cent.

How far the quantitative estimates of mineral composition in this clay are accurate can very well be questioned. In fact it is quite difficult to say whether the estimated minerals reflected the X-rays exactly in the same manner as the known binary mixtures, since the degree of crystallinity and chemical composition could have been quite different in them.

INTERPRETATION OF DIFFERENTIAL THERMAL CURVES

The individual mineral components of the clay could not be identified from their differential thermal curves (whole sample and less than 2 microns fraction) with any certainty, because the characteristic thermal peaks could be interpreted in several ways or the mineral reaction of one was not obvious in the presence of another. For example, the characteristic endothermic reaction at 540°C (differential thermal curve of the whole sample) could be attributed to kaolinite and montmorillonite, but with all probability this dehydroxylation peak was more due to a montmorillonitic (expanding-lattice) mineral. The latter was confirmed by a large initial endothermic peak at 125°C (differential thermal curve of less than 2 microns fraction) due to the removal of

interlamellar or adsorbed water. This low temperature peak system is not shown by kaolin minerals (excepting halloysite-hydrated variety), but exists invariably in three-layer lattice clay minerals (montmorillonoids, micas). Further, this clay was saturated with divalent cations (Ca^{++}, Mg^{++}), for it showed another loop (endothermic reaction) at about 160°C. It shows that unit sheets held calcium or magnesium ions which adsorbed two molecular layers of water and resulted in a spacing of 15·08 Å. As kaolinite formed about one fourth of the total mineral composition (X-ray evidence) of the less than 2 microns fraction a comparative lower endothermic peak at 540°C (for well crystallised kaolinite the endothermic peak is at about 600°C) corresponding to the loss of OH water from the mineral lattice, reflected a smaller particle size and crystallinity of the mineral. This peak was followed by an exothermic reaction (whole samples as well as clay fraction) at about 950°C, which could be due to kaolinite or montmorillonite.

"ABNORMAL MONTMORILLONITE"

It will be observed from the above that the main dehydroxylation peak in the 550°C region has been attributed to a montmorillonitic mineral, which is rather ususual, because a

'normal' montmorillonite gives its main endothermic peak due to dehydroxylation at about 700°C. The latter is true of 'Wyoming bentonite' and other bentonitic materials having an order of stacking of layers and the crystal organisation and characterised by a diagnostic endothermic peak at 700°C.

This deviation (from 700°C to 550°C) of the main endothermic peak by 150°, present in such montmorillonitic rich clay is of great interest. Undoubtedly a similar endothermic peak at 550°C is characteristic for nontronite (Kerr, Kulp and Hamilton 1949), the iron analogue of montmorillonite in which there is practically a complete replacement of Al^{+++} by Fe^{+++} in the Octahedral coordination. However, it is necessary to carry out the 'Greene -Kelley test' (1952, 1953) which enables one to distinguish the specific members of the montmorillonoids particularly between montmorillonite and nontronite. The test (explained earlier), however, did not support the presence of nontronite. Besides, the substitution of iron alone does not seem to be the cause of a lower main dehydroxylation peak (Sudo and Ota 1952) in an iron rich montmorillonite. So, whatever may be an explanation or correlation for a lower dehydration reaction in this type of montmorillonite, is discussed in detail

at the end of this chapter. For the time being and hereafter such an anomalous montmorillonite will be referred to as an "abnormal montmorillonite", which on X-ray examination showed the characteristic reflections of about 18·19 A (glycerol-montmorillonite) of a normal dioctahedral montmorillonites, although its differential thermal curve is not in agreement with those described in literature (Kerr, Kulp and Hamilton 1949).

QUANTITATIVE ESTIMATION OF MINERALS FROM DIFFERENTIAL THERMAL CURVES

Since it was impossible to establish the identity of each mineral component from the differential thermal curves, no attempt was made at quantitative evaluation or any correlation from the X-ray results. It is very difficult to interpret from a differential thermal curve alone as to how far these dehydroxylation peaks reflect the individual mineral components particularly when they are associated with abnormal montmorillonite which has a peak overlapping those of poorly crystallised kaolinite, illites and nontronites.

CONCLUSION FROM THE DIFFERENTIAL THERMAL METHOD

With all the difficulties and limitations in the

differential thermal method of analysis, the method gives conclusive information about the stacking of sheets in order and disorder structure of minerals. In the writer's opinion the method has been of an interest and has proved very useful in revealing structural irregularity of chemical composition (?) of abnormal montmorillonite, which could not be determined by X-ray diffraction method alone.

CLAY FROM GLENORA (1A)

Table 3 - X-ray diffraction measurement data
(Ni filtered, copper K radiation)

Whole Sample (wedge-powder) (film recorded)					
Untreated		Treated with glycerol		Heated to 600°C	
I	d	I	d	I	d
s	16·16	vs	19·17	mw(di)	9·85
vvw	4·92	vvw	5·56	mw	4·46
ms	4·46	vw	4·45	mw	4·26
ms	4·23	mw	4·17	s	3·33
vs	3·32	ms	3·32	mw(b)	2·71
vw	2·68	vw	2·71	mw(b)	2·52
mw	2·56	mw	2·58	vvw	2·12
m	2·44	mw	2·43	vvw	1·98
vbr(di)	(2·27 (2·14	vw	1·80	mw	1·81
mw	1·80	vw(di)	1·71	vw(di)	1·67
vw(di)	1·72			vvw(di)	1·53
		vw(di)	1·66		
vw(di)	1·66			mw	1·45
		vvw(di)	1·54		
vvw(di)	1·55			mw	1·38
		vvw	1·49		
vvw	1·49				
mw	1·37	mw	1·37		

Key to abbreviations used - same as Table 2

(b) = broad

CLAY FROM GLENORA (1A)

Table 3 - continued

Oriented Aggregates (film recorded)					
Untreated		Treated with glycerol		Heated to 600°C	
I	d	I	d	I	d
vw(di)	14·51	vw(di)	17·31	vw	9·92
vvw	10·12	vvw	9·03?		?
m	6·99	w	6·98		
vvw	5·26	vvw	6·40		?
vvw	4·86	vw	5·24	w	3·29
vw	4·33	vw(di)	4·92	mw	3·18
m	4·13	vvw(di)	4·45	w(di)	2·67
vw	3·61	m	4·10	w(di)	2·48
m	3·51				
ms	3·29				
vw	3·10				
w	2·73				
w	2·64				
vw(di)	2·51				
mw	2·41				
vvw (band)	2·25				
vvw	2·13				
vvw (band)	2·04				
vvw	1·88				
vvw	1·78				
vw	1·69				

(?) = could not be measured

Minerals Identified

The mineral determinations were based mainly on the results obtained from clay sample (1) and for their quantitative estimates the reflections were compared with those of the standard binary mixtures and the X-ray diffraction patterns of clay (1).

The following minerals, in order of abundance were identified from their characteristic reflections explained in clay (1). Abnormal montmorillonite 60 per cent (greater than 1), quartz 20 per cent (less than 1), kaolinite and illite (oriented aggregate) present scantily up to 10 per cent were characterised by their oriented lines at 6·99 Å and 10·12 Å respectively. There was a suggestion of the presence of goethite from the X-ray examination (whole sample) characterised by the lines at 4·92 Å (with very very weak intensity) and 2·68 Å (with very weak intensity). The mineral goethite was confirmed by taking the X-ray diffraction photograph of heated (600°C) whole sample where it decomposed to haematite. The X-ray powder pattern gave the characteristic reflections at 2·71 Å and 2·51 Å with a broadening effect (intensity) which showed a smaller crystal size. However, it could not be detected from the differential thermal curves due to

the absence of its characteristic endothermic peak at about 390°C. Further, the sensitivity of the differential thermal method of analysis (particularly for calcite, gibbsite and goethite) suggested that goethite, though identified by X-ray examination, could not be present in more than traces (less than 1%). Gibbsite was identified by its characteristic endothermic peak at about 320°C and its quantitative estimate was 5 per cent. However, it remained undetected by X-ray diffraction. The rest of the interpretation from the differential thermal curves was quite similar to clay (1) for abnormal montmorillonite.

Conclusion may be made from a comparison of the diffraction patterns of the untreated and glycerol treated oriented aggregates, regarding the peculiarities of the line profiles and their intensities of abnormal montmorillonite. The basal spacing (001) at 14·51 Å shifted to 17·31 Å for the glycerol treated oriented aggregate, enhanced intensity. In a normal montmotillonite the relative change in intensity between an untreated and glycerol treated orineted aggregate is quite diagnostic (MacEwan 1946). The above mentioned character suggests a structural difference in the abnormal montmorillonite which is the dominant mineral constituent of clay (1A).

CLAY FROM PLENTY (3)

Table 4 - X-ray diffraction measurement data.
(Ni filtered, Cu Kα radiation)

Whole Sample (Wedge-powder) (film recorded)					
Untreated		Treated with glycerol		Heated to 600°C	
I	d	I	d	I	d
ms(di)	15·32	s(di)	16·46	vw(di)	10·63
vw	7·43	vw	7·43	w	4·48
w	4·48	w	4·48	w(sp)	4·15
w(sp)	4·27	vw(sp)	4·15	vvw(sp)	3·82
w(sp)	3·70				
w	4.0	vw	3.78	s(sp)	3.34
s(sp)	3.35	s(sp)	3.32	vvw(sp)	2.94
w(sp)	3.2	w(sp)	3.18	w(sp)	2.50
w	2.55	w	2.57	vvw(sp)	2.26
w(sp)	2.11	w	2.37	w(sp)	2.11
vvw(sp)	1.96	vw(sp)	2.25	vvw(sp)	1.94
vw(sp)	1.80	vw	2·12	vvw	1·81
vvw(sp)	1·67	vw	1·81	vvw	1·65
vvw	1·53	vvw	1·66	vw(sp)	1·37
vw(sp)	1·49	vvw	1·53	vvw	1·24
vw(sp)	1·37	vw(sp)	1·49		
		vw(sp)	1·36		

CLAY FROM PLENTY (3)

Table 4 - continued

Oriented Aggregates (film recorded)					
Untreated		Treated with glycerol		Heated to 600°C	
I	d	I	d	I	d
vw(di)	13 37	w(di)	17 70	mw	10 12
w(di) ?	7 52	w	7 45	m	4 40
m(di)	4 50	m(di)	4 37	mw	3 50
w	3 59	w	3 51	mw	3 32
w	3 36	vvw	3 36	w(di)	2 57
m	2 54	m	2 54	w(di)	1 70
mw	2 42	mw	2 37	w(di)	1 53
mw	1 69	mw	1 67		
mw	1 50	mw	1 49		
vvw(di)	1 31	mw	1 29		

Key to abbreviations used: Same as Table 2

(?) = unorientated

Mineral Identifications

The results of the identifications showed a mixture of abnormal montmorillonite 60 per cent and quartz 20 per cent as the predominant minerals. Abnormal montmorillonite was identified by the presence of a medium strong reflection at

15·32 Å, which expanded to 16·46 Å with glycerol treatment and collapsed to a spacing at 10·63 Å on heating the clay to 600°C. Quartz was characterised in the same way as described for the clays from Glenora (1 and 1A). The kaolin minerals were clearly indicated by the presence of reflections at 7·52 Å and 7·43 Å in the aggregate and wedge-powder photographs. The basal reflection (001) for metahalloysite is of the order 7·4 - 7·5 Å. Since this reflection (001) had a comparatively higher interplanar spacing that kaolinite at 7·52 Å and unorientated lines (001) and (002) at 7·52 Å and 3·59Å, the mineral present was metahalloysite. The basal spacing (001) did not form an organic complex (MacEwan 1946). The very weak intensity of these lines proved that it was present scantily - 10 per cent. Feldspar, present up to 5 per cent, was identified by lines at 3·7 Å and 4·0 Å with weak intensity in the wedge-powder photograph.

The interpretations from the differential thermal curves were the same as described for clay sample (1).

CLAY FROM MACQUARIE PLAINS (16)

The mineralogy of clay from Macquarie Plains as

determined by both X-ray and differential thermal analysis showed predominantly abnormal montmorillonite above 60 per cent (greater than in 1, 1A and 3) and quartz 25 per cent with minor amounts of feldspar (5 per cent) kaolinite (less than 5 per cent) and traces of mica or illite (as revealed in the oriented aggregate) and organic matter (present in less than 2 micron fraction).

The interpretation of differential thermal curves revealed a strong endothermic peak between 150° and 200°C due to the removal of interlamellar water, a characteristic of montmorillonoids. An exothermic hump at about 330°C showed traces of organic matter present in the fine fraction of the clay.

It was observed that the clay was very rich in montmorillonite from the X-ray examination, but was characterised by a prominent dehydroxylation peak at about 535° - 550°C, followed by a broad exothermic reaction at 930°C, reflecting strongly the anomalous montmorillonite.

CLAY FROM NEW NORFOLK (2)

Table 5 - X-ray diffraction measurement data
(Ni filtered, Cu K_a radiation)

Whole Sample (wedge-powder) (film recorded)					
Untreated		Treated with glycerol		Heated to 600°C	
I	d	I	d	I	d
vvw(di)	15.47?	wvw(sp)	6.01	vw(di)	9.94
vvw(sp)	6.24	m(sp)	4.22	m(sp)	4.23
m(sp)	4.45	m	3.75	w(sp)	3.71
vvw(sp)	4.31	vs(sp)	3.33	vs(sp)	3.36
vvw	4.06	m(sp)	3.18	vw(sp)	3.16
vvw	3.79	w(sp)	2.94	vvw(sp)	2.55
vs(sp)	3.38	w	2.58	vvw	2.42
m(sp)	3.28	m(sp)	2.44	vw(sp)	2.24
w(sp)	3.01	m	2.27	w(sp)	2.09
w	2.64	m	2.13	w	1.96
w	2.59	m	1.96	m(sp)	1.80
m(sp)	2.50	m	1.80	m	1.65
m	2.31	m	1.66	m	1.52
w(sp)	2.26	m	1.53	m	1.44
vw(sp)	2.03	m	1.44	w(sp)	1.36
m(sp)	1.83	w(sp)	1.37	w	1.28
vw(sp)	1.70			w	1.21
m(sp)	1.55				
w(sp)	1.39				
w	1.2				
w	1.18				

CLAY FROM NEW NORFOLK (2)

Table 5 - continued

Oriented Aggregates (film recorded)					
Untreated		Treated with glycerol		Heated to 600°C	
I	d	I	d	I	d
m(di)	14·60	ms(di)	17·70	vw	9·70
m	7·19	vvw	10·0	vvw	4·49
vw(di)	4·91	w	7·08	w	4·25
vvw(di)	4·44	vw	4·44	s	3·32
m	4·23	w	4·14	vw	3·23
m	3·53	m	3·50	vvw	2·95
s	3·30	s	3·30	vvw	2·71
vvw	3·2	vvw	2·97	w	2·49
vvw	2·58	vvw	1·82	vw	2·26
vvw	2·00	vvw	1·69	vw	2·11
vw	1·82	vvw	1·51	vw	2·04
vvw	1·69	vw	1·37	mw	1·82
vvw	1·50			w	1·67
				w	1·53
				w	1·36

Key to abbreviations: Same as Table 2

Minerals Identified

The minerals identified in order of abundance, by their characteristic reflections, were mainly quartz

70 per cent, feldspar 10 per cent, abnormal montmorillonite 10 per cent, and kaolinite 5 per cent. The less than 2 microns fraction contained quartz 40 per cent, abnormal montmorillonite 30 per cent, kaolinite 20 per cent and mica less than 10 per cent.

The differential thermal curve of the clay (whole sample) did now show much evidence of any characteristic reactions, since the clay contained very small amounts of clay minerals. However, broad loops at 100°C and 540°C showing endothermic reactions reflected the three layer type minerals. The differential thermal curve of the less than 2 microns fraction was the same as described for the earlier clay samples.

CLAY FROM CLAREMONT; WINDERMERE BEACH (4)

Table 6 - X-ray diffraction measurement data
(Ni filtered, Cu K_a radiations)

Whole Sample (wedge-powder) (film recorded)					
Untreated		Treated with glycerol		Heated to 600°C	
I	d	I	d	I	d
m	7·34	m	7·29	mw	4·43
mw	4·43	mw	4·42	m	4·25
m	4·24	m	4·25	vvw	3·54
mw	3·57	w	3·54	vs	3·32
vs(sp)	3·34	vs(sp)	3·33	m	2·47
vw	3·00	vw	3·00	w	2·27
mw	2·61) 2·44)	mw	2·58) 2·44)	w	2·24
				vvw	2·11
mw	2·39) 2·30)	mw	2·35) 2 28)	mw	1·98
vw	2·21	vw	2·22	m	1·81
mw	2·13	mw	2·12	m	1·66
mw	1·98	mw	1·98	mw	1·53
m	1·81	m	1·83	s	1·37
mw(di)	1·66	m	1·81		
m	1·53	mw(di)	1·66		
mw	1·49	m	1·53		
mw	1·44	mw	1·49		
s	1·37	mw	1·44		
mw	1·28	s	1·37		
mw	1·25	w	1·28		
		w	1·25		

CLAY FROM CLAREMONT, WINDERMERE BEACH (4)

Table 6 - continued

Oriented Aggregates (Film Recorded)					
Untreated		Treated with glycerol		Heated to 600°C	
I	d	I	d	I	d
w(di)	12.17	vs(di)	17.7	mw	10.01
vs	7.15	vs	7.10	vvw	5.0
vvw	4.32	vvw	4.36	vvw	4.40
m	4.20	m	4.24	s	4.25
vs	3.54	vs	3.53	w	3.38
vs	3.32	vs	3.31	vs	3.32
mw	2.56) 2.47)	mw	2.56) 2.41)	vvw	3.25
				mw	2.46
mw	2.39) 2.28)	mw	2.39) 2.27)	vvw	2.26
mw	2.12	mw	2.11	w	2.13
w(di)	1.99	w(di)	1.99	w	2.00
mw	1.81	mw	1.80	w	1.82
w(di)	1.67	w(di)	1.66	w	1.67
m	1.53	mw	1.53	mw	1.54
		mw	1.49	w	1.37
		mw	1.37		

Key to abbreviations used: Same as Table 2

Minerals Identified

The X-ray and differential thermal analysis examinations showed thatthe clay contained a mixture of quartz 50 per cent, kaolinite 40 per cent, abnormal montmorillonite 10 per cent, calcite 1-2 per cent, and traces of organic matter or pyrites.

A line at 4·43 Å (whole sample, heated to 600°C) was due to meta kaolinite structure suggesting that the kaolinite structure was not completely destroyed by heating the clay to 600°C. Another line at 3·00 Å, of very weak intensity, was due to calcite.

The differential thermal curve of the whole sample gave a very weak endothermic reaction at about 100°C which was due to the loss of adsorbed water present in the 3 layer type minerals. A large symmetrical endothermic peak at about 560°C and an exothermic peak at 930°C were typical reactions of kaolinite. However the lower heat of reactions at 560°C reflected a poor crystallinity of the clay mineral. Its content (Carthew 1955) was determined approximately from the area of the endothermic peak (since there is no direct method available of assessing its degree of crystallinity and correlating

this factor with the area under the endothermic peak) and it was nearly 40 per cent. A broad exothermic hump at 340°C showed the presence of traces of organic matter or pyrites and another endothermic loop at 875°C revealed traces of calcite.

CLAY FROM CORNELIAN BAY (5)

Table 7 - X-ray diffraction measurement data
(Ni filtered, Cu Kα radiation)

Whole Sample (wdege-powder)
(film recorded)

Untreated		Treated with glycerol		Heated to 600°C	
I	d	I	d	I	d
s(di)	15.31	s(di	19.60	mw(di)	10.26
mw	7.36	mw	7.36	ms	4.45
w	4.48	w	4.44	s(sp)	4.23
m(sp)	4.27	m(sp)	4.27	mw	3.71
vvw	3.70	vvw	3.70	vs(sp)	3.32
s(sp)	3.33	s(sp)	3.33	vw	3.2
vw	3.20	vw	3.20	vw	2.59
mw	2.59) 2.46)	mw	2.59) 2.46)	mw(sp)	2.45
				m	2.26
w	2.39) 2.29)	w	2.39) 2.29)	vw	2.23
mw(sp)	2.12	mw(sp)	2.12	m	2.13
mw	1.99	mw	1.99	m	1.98
m(sp)	1.81	m(sp)	1.81	m	1.81
w	1.67			mw	1.67
m	1.54			m	1.53
w	1.49			m	1.44
w	1.45			s	1.36
m	1.37				

CLAY FROM CORNELIAN BAY (5)

Table 7 - continued

Oriented Aggregates (film recorded)					
Untreated		Treated with glycerol		Heated to 600°C	
I	d	I	d	I	d
vs(di)	13.74	vs(di)	17.36	ms	9.92
vw	10.24	vw(di)	9.21 ?	mw	4.92
vs	7.21	vs	7.15	mw	4.46
m	5.07	vvw	5.76	m	4.27
mw	4.40	vvw	5.01	vw	3.73
m	4.24	mw	4.40	vw	3.50
vvw	<u>3.95</u>	m	4.26	vs	3.34
vs	3.57	vvw	<u>3.95</u>	vw(di)	3.23
vs	3.33	vs	3.57	mw	2.46
mw	3.11) 3.10)	vs	3.32	mw	2.30
				vw	2.24
mw	2.54) 2.45)			mw	2.14
mw	2.37) 2.29)				
vvw	2.25				
m	2.12				
m(di)	1.98				
m	1.82				

Key to abbreviations used:

Underlined d values are β reflections

? = mica and abnormal montmorillonite (002)

Minerals Identified

This clay from Cornelian Bay is very similar to clay (1) in mineral composition. It contained abnormal montmorillonite 40 per cent, quartz 30 per cent, kaolinite 25 per cent and feldspar less than 5 per cent. The less than 2 microns fraction contained a high proportion of clay minerals - abnormal montmorillonite 60 per cent, kaolinite 30 per cent, illite 5 per cent and quartz less than 10 per cent.

The differential thermal curves were the same as those described for clay (1).

CLAY FROM LAWRENNY (6)

Minerals Identified

The minerals identified by their characteristic reflections were quartz 50 per cent and kaolonite 40 per cent, with minor amounts of mica or illite (less than 5 per cent) and chlorite present in traces only.

A chloritic mineral was recognized in the less than two microns fraction of the aggregate on the basis of 13.96 Å reflection (001) which remained unexpanded with glycerol and gave a much sharper first order basal reflection by heating the

aggregate to 600°C.

The differential thermal curve revealed a very poorly developed low temerpature endothermic peak (100°C). A high temperature endothermic peak at 800°C was also absent therefore the identification of chlorite was only from the X-ray examination of the oriented aggregate. However, there was strong evidence of kaolinite (discussed in 4) probably of medium crystallinity.

CLAY FROM LAWRENNY (7)

Minerals Identified

The mineral composition as determined showed that the Lawrenny clay is a highly siliceous kaolinitic clay containing a very small amount of illite, hydrobiotite or montmorillonite. The percentage composition is quart 50, kaolinite 40 and the three layer minerals 5-10.

The appearance of 10.23 Å line in the X-ray photograph of the heated 'whole sample' was due to the presence of either micas or montmorillonite. It was also shown in the differential thermal curves by the presence of a broad endothermic loop at about 100°C.

CLAY FROM FENTONBURY (8)

Table 8 - X-ray diffraction measurement data
(Ni filtered, Cu Ka radiation)

Whole Sample (wedgepowder) (film recorded)					
Untreated		Treated with glycerol		Heated to 600 C	
I	d	I	d	I	d
m(di)	15.37	ms(di)	18.51	vvw(di)	9.92
ms	7.20	ms	7.17	ms	4.51
vvw	5.05	ms	4.43	ms	4.27
ms	4.44	ms	4.25	vs	3.35
ms	4.25	m	3.53	vw	2.62
mw	3.52	s	3.34	vw	2.47
s	3.35	mw(band)	2.56) 2.46)	vw	2.34
mw(band)	2.56) 2.44)	mw (band)	2.35) 2.29)	vvw	2.26
				vw	2.13
mw(band)	2.36) 2.29)	vvw	2.23	vw	1.97
vvw	2.24	w	2.13	w	1.81
w	2.13	w	1.98	vw(di)	1.67
				w	1.54
w	1.98	m	1.96		
				w	1.37
ms	1.81	w	1.67		
mw	1.67	w	1.53		
w	1.54	w	1.49		
w	1.49	ms	1.37		
ms	1.38				

Key to abbreviation used - Same as Table 2

CLAY FROM FENTONBURY (8)

Table 8 - continued

Oriented Aggregates (film recorded)					
Untreated		Treated with glycerol		Heated to 600°C	
I	d	I	d	I	d
vs(di)	14.85	vs(di)	17.57	w(di)	9.97
vvw	9.97	band	10.12	vvw	4.44
vs	7.23	vs	7.15	mw	4.26
m	4.97	ms	4.25	s	3.34
vvw	4.39	vvw	3.93 (β)	w	2.45
ms	4.21			w	2.12
		vs	3.53		
vvw	3.92 (β)			vw	1.98
		vs	3.33		
				w	1.82
vs	3.52	mw(band)	2.52) 2.43)	vw	1.67
vs	3.32				
		mw(band)	2.36) 2.29)	mw	1.54
mw(band)	2.53) 2.44)			m	1.38
		vvw	2.20		
mw(band)	2.37) 2.30)	w	2.11		
vvw	2.23	w	1.79		
w	2.12	vw	1.66		
vw	1.98				
w	1.80				
vw	1.66				
w	1.53				
vvw	1.49				
vvw	1.45				
mw	1.37				

Minerals Identified

The minerals identified in order of abundance from the X-ray examination and differential thermal analysis were kaolinite 40 per cent, quartz 35 per cent, abnormal montmorillonite 20 per cent and illite less than 5 per cent (as revealed by an oriented (001) reflection at 10.12 Å)

The differential thermal curve was typical of kaolinite and its quantitative determination has already been discussed.

CLAY FROM DUNROBIN BRIDGE (9)

Table 9 - X-ray diffraction measurement data
(Ni filtered, Cu Kα radiation)

Whole Sample (wedge-powder) (film recorded)					
Untreated		Treated with glycerol		Heated to 600°C	
I	d	I	d	I	d
ms	7.26			ms	2.67
ms	4.87			ms	2.50
ms	4.44			vvw	2.18
ms	4.21			vvw	1.84
m	3.67			w	1.68
vw	3.41			vvw	1.60
vvw	3.29			vw	1.47
ms	2.75			vw	1.45
ms	2.59				
vvw	2.47				
vvw	2.40				
vvw(di)	2.37				
vvw	2.02				
vvw	1.87				
w(di)	1.71				
w	1.51				
w	1.47				

No change with glycerol treatment

CLAY FROM DUNROBIN BRIDGE (9)

Table 9 - continued

Oriented Aggregates (film recorded)				
Untreated		Treated with glycerol	Heated to 600°C	
I	d		I	d
ms	7.07	No change with glycerol treatment	ms	2.76
s	4.75		ms	2.55
ms	4.29		vvw	2.48
w	4.16		vvw	2.23
ms	3.54		vvw	1.89
vvw	3.30		vvw	1.50
vvw	3.18		vvw	1. 48
w	2.66			
vvw	2.50			
vvw	2.42			
band	2.17			
vvw	2.03			
vvw	1.98			
vvw	1.91			
band	1.68			

Key to abbreviation used: Same as Table 2

Minerals Identified

The minerals identified were kaolinite 60 per cent and gibbsite 30 per cent with minor amounts of goethite 5 per cent and haematite 1 - 5 per cent only.

Gibbsite was identified in the X-ray diffraction pattern on the basis of reflections at 4.87 Å 4.44 Å and 2.47 Å respectively.

The differential thermal curves revealed two prominent endothermic peaks at 340°C and 575°C respectively. The former at 340°C is due to gibbsite and the latter at 575°C is attributed to kaolinite. The area under the endothermic peaks was used for the quantitative estimation of these two minerals. There was no separate endothermic reaction due to goethite, because of the overlapping peaks of goethite and gibbsite.

CLAY FROM KENMERE HILL, OUSE (12)

Minerals Identified

The minerals identified from their characteristic reflections and differential thermal analysis, were a highly crystallized kaolinite 85 per cent, with minor amounts of haematite

10 per cent, gibbsite 5 per cent and traces of goethite.

The mineral haematite was identified on the basis of reflections at 2.68Å(mw) and 2.50 Å and it was confused with goethite which gives almost similar reflections. But the absence of any sharp prominent endothermic peak in the differential thermal curve confirmed haematite. However a small endothermic loop at about 360°C showed the presence of traces of goethite as well. A line of very weak intensity at 4.86 Å was attributed to gibbsite. But more than 5 per cent could not be present because the area below the endothermic peak at about 290°C was extremely small. The presence of a shaper symmetrical endothermic peak at 580°C followed by an intense exothermic reaction at about 960°C reflected a well-crystallized kaolinite.

CLAY FROM SANDY BAY, HOBART (10)

Table 10 - X-ray diffraction measurement data
(Ni filtered, Cu Kα radiation)

Oriented Aggregates (film recorded)					
Untreated		Treated with glycerol		Heated to 600°C	
I	d	I	d	I	d
ms(di)	15.11	s(di)	18.07	vs	9.87
w	10.33	w	10.58	s(band)	4.82
m	7.23	s(di)	8.87	vw	4.51
vvw	4.94	vs	7.23	s	4.29
vvw	4.42	w(band)	5.84	vvw	3.73
m	4.22	w	4.96	vvw	3.48
vs	3.57	ms	4.42	vs	3.35
vs	3.33	ms	4.24	s(di)	3.25
mw	3.03	vs	3.57	w	3.04
vw(band)	2.94) 2.70)	vs	3.34	w(band)	2. 75
		ms(di)	3.03	m(band)	2.58) 2.41)
vw(band)	2.62) 2.48)	w	2.55		
vw	2.38	w	2.45	m(band)	2.27) 2.13)
vvw	2.29	w	2.35	vvw	2.03
vvw	2.13	vw(di)	1.98	w	1.82
vvw	2.01	vw	1.83	vw	1.68
vvw	1.82	vw	1.67	vw	1.53
vw	1.54	vvw	1.55	vw(band)	1.46
vw	1.48	vw	1.50	vw	1.41

Key to abbreviations used - Same as Table 2

Minerals Identified

The X-ray and differential thermal analysis examination showed that the clays (very similar to 3) contained a mixture of abnormal montmorillonite 60 per cent, quartz 20 per cent, kaolinite 10 per cent, illite 5 per cent, calcite 1-5 per cent and traces of feldspar (whole sample).

Calcite was identified on the basis of a line at 3.04 Å with a weak intensity. The mineral was confused with illite since the latter gives a similar reflection at about 3.08 Å. But the intensity of the line at 3.04 Å was too high compared with the intensities of other illite reflections present in X-ray diffraction pattern of the heated and untreated aggregate. Besides, the differential thermal curve showed a prominent endothermic loop at about 865°C (in clay fraction) due to calcite. The other endothermic peaks at 100°C and 560°C were due to abnormal montmorillonite and kaolinite.

CLAY FROM SANDY BAY, HOBART (11)

This clay is from the drill hole (described in an earlier chapter) and same profile as (10). It was characterised by abnormal montmorillonite 55-60 per cent, quartz 25-30 per cent,

kaolinite 10-15 per cent, illite 5 per cent, with traces of feldspar, calcite and organic matter.

The only variations in mineral composition found between (10) and (11) were in their quantitative estimates. The latter contained slightly more quartz and kaolinite and a little less abnormal montmorillonite than (10).

The differential thermal curve showed a broad exothermic hump between 300° and 400°C due to the presence of organic matter.

The conclusion may be draw from the composition of clays (10) and (11) that no significant clay mineral variation existed in the different horizons of these lacustrine sediments and the occurrence of organic matter in clay (11) was quite independent of the clay mineral composition.

CLAY FROM Q/MP 105 (13)

Minerals Identified

The minerals identified were mainly quartz 50 per cent and kaolinite 30 per cent with minor amounts of montmorillonite (?) or mixed layer minerals (?) 10 per cent, feldspar 5 per cent and illite less than 5 per cent.

The first order (001) basal reflection at about 14.0 Å was not clearly visible in the oriented aggregate pattern and the glycerol treated aggregate remained unchanged. However the heated aggregate photograph showed a strong mica line at about 10 Å, which could be attributed to a montmorillonoid and/or mixed layer mineral, in addition to the (001) basal reflection from illite. The presence of a montmorillonite-type or mixed-layer mineral was also supported by a large low temperature endothermic reaction (present in clay fraction) at 100°C due to the loss of interlayer water. A large symmetrical endothermic peak at about 560°C followed by an exothermic peak at 920°C was due to kaolinite.

CLAY FROM DUNALLEY CANAL (14)

Minerals Identified

The mineral composition as determind from the X-ray and differential thermal analysis showed a similarity to (3). The clay (14) contained a mixture of kaolinite 45 per cent and quartz 40 per cent, with montmorillonoid or swelling chlorite about 10 per cent and illite 5 per cent.

The clay sample presented considerable difficulty

in identifying a mineral responsible for the line at 14 Å (001), which could be due to a montmorillonite-type mineral or a swelling chlorite. The first order (001) reflection at 14 Å shifted to 18 Å with glycerol treatment. This change of spacing suggested a montmorillonite-type mineral or a swelling chlorite (Stephen and MacEwan 1949). Besides, the chlorite was also confused with kaolinite, since the second order (002) basal reflection of the former at 7 Å was close to the corresponding first order (001) basal reflection from kaolinite. The X-ray pattern of the heated oriented aggregate showed a line at about 10 Å, which could be due to a montmorillonite-type mineral and illite. But the disappearance of the 14 Å line from the heated aggregate did not necessarily support the absence of the swelling type of chlorite as a constituent of the clay, because examples are known of poorly crystalline clay materials having chlorite, in which the 14 Å line does not appear on heating the clay to 600°C (Personal communication from W. F. Cole)

CLAY FROM MANGALORE (B) (15)

Minerals Identified

The X-ray diffraction photographs were compared to

samples 1, 1A, 3 and 5, which have already been described.

The characteristic reflections showed the presence of abnormal montmorillonite 40 per cent, kaolinite 40 per cent, and quartz 15-20 per cent.

The differential thermal curves were the same as those described for clay (1) and the minerals identified by the X-ray examination could not be interpreted from their differential thermal curves.

CLAY FROM MANGALORE (B) (18)

Minerals Identified

This clay provided very poor diffraction patterns of the 'wedge-powder' sample, therefore, the minerals present could not be identified with any certainty, particularly in their quantitative estimates. Even a mineral like quartz could not be determind quantitatively, although it gives very strong, sharp reflections when present as low as one per cent in a clay. The factor responsible for such uncertainty in estimating the mineral content may be the presence of a mineral (calcite) which strongly absorbs the X-rays and/or the presence of an amorphous material on the crystalline particles which may reduce the

reflected intensity on account of its non-crystalline and absorptive character. These limitations did not allow the correct measurements of the intensities of the X-ray reflections in the patterns, so estimation of the relative amounts of the mineral components was not attempted. However, a combined X-ray and differential thermal analysis examination revealed quartz (quantity ?) kaolinite 20 per cent (from differential thermal curve interpretation), abnormal montmorillonite (quantity ?) identified by the presence of interlamellar water and a low temperature endothermic peak and traces of calcite (?) (the presence of calcite could not be confirmed due to the absence of the characteristic endothermic peak at about 875°C). Furthermore, the differential thermal analysis showed that the kaolinite was poorly crystallized due to the reduced size and rounded shape of the exothermic peak.

The less than 2 microns clay fraction in the oriented aggregate photographs showed qualitatively a high proportion of clay minerals in this order: Kaolinite, abnormal montmorillonite, quartz and illite.

CLAY FROM ONE TREE POINT, SANDY BAY (19)

Minerals identified

This clay could be compared to samples 1, 1A, 3, 10, 11 and 16 in mineral composition.

The predominant mineral, abnormal montmorillonite (60 per cent) was identified on the basis of the 14 Å spacing which expanded to about 18 Å upon glycerol treatment. The differential thermal curve did not show the characteristic endothermic peak for a normal montmorillonite. Quartz, between 25 and 30 per cent, was identified by the presence of strong lines at 4.22 Å, 3.37 Å and 1.81 Å. A very weak reflection at 7 Å which disappeared upon heat treatment (wedge-powder photograph) was due to kaolinite (5 and 10 per cent). Illite (about 5 per cent) was identified by the presence of first order (001) baaal interplanar spacing of about 10 Å in the oriented aggregate pattern extent. Feldspar was present in traces only and identified by a very very weak line at 3.2 Å (wedge-powder X-ray pattern).

CLAY FROM LAUNCESTON (17)

Minerals Identified

The X-ray diffraction patterns of this clay were compared to those of clay (6). The minerals identified by their characteristic interplanar spacings showed that the clay

is highly siliceous kaolinitic one with an extremely small amount of illite. The percentage composition is quartz 50, kaolinite 45 and illite less than 5.

The differential thermal curve of the 'whole sample' showed a sharp low temperature endothermic peak, suggesting that the sample was probably wet. This large peak could not be due to the loss of adsorbed water present in the 3 layer type minerals, because no such minerals in any appreciable amount were identified by the X-ray examination. However, illite (present in minor amount) was identified in the oriented aggregate photograph on the basis of the first order basal reflection at about 10 Å of very weak intensity. But on heating the aggregate to 600°C the 10 Å line showed a definite sharpening, which could be due to the presence of additional, more highly hydrated layers interpolated between the illite sheets. The differential thermal curve of the less than 2 microns fraction showed a broad interlayer water effect and proved the characteristic endothermic and exothermic reaction of kaolinite at 585°C and 950°C respectively. Further, the shape and size of the peaks revealed that kaolinite was well-crystallized and an abundant clay mineral constituent of the clay.

CLAY FROM LAUNCESTON (25)

Minerals Identified

The X-ray and differential thermal analysis examination of the clay showed a lot of similarity to clays (4, 6 and 17). The minerals identified were mainly quartz 50 per cent and kaolinite 40 per cent with muscovite mica 5 per cent, montmorillonoid less than 5 per cent and gibbsite (?) about 1-2 per cent.

Mica showed a series of basal reflections on oriented aggregate photograph at 10 Å, 5.0 Å and 3.3 Å. The muscovite type was identified by the presence of a strong second order (002) basal reflection and medium intensity lines between 3.2 Å and 2.8 Å. (Nagelschmidt 1937). Gibbsite was identified by the presence of a very very weak line at 4.82 Å present in the wedge-powder pattern. It remained unconfirmed because of the absence of the characteristic endothermic peak at about 320°C. However, the differential thermal curves showed a broad endothermic loop between 200° and 300°C, which could be due to gibbsite.

CLAY FROM LAUNCESTON (26)

Minerals Identified.

The X-ray diffraction patterns and differential thermal curves were compared with those of samples 4, 6, 17 and 25. The characteristic reflections showed mainly quartz 60 per cent and kaolinite 35 per cent with abnormal montmorillonite less than 5 per cent, illite 1-5 per cent and gibbsite about 1-2 per cent.

CLAY FROM BRUMBY CREEK AREA (24)

Minerals Identified

The mineral composition as determined was very similar to No. (26) - quartz 60 per cent, kaolinite 35 per cent, illite less than 5 per cent, abnormal montmorillonite about 5 per cent. Furthermore, the differential thermal curve (whole sample) showed an exothermic peak at about 300°C due to the presence of organic matter.

CLAY FROM OLD BEACH ROAD (20)

Table 11 - X-ray diffraction measurement data
(Camera: Philips large 5.73 cm.)
Exposure time: 16 hours.

(UNICAM.) Whole Sample (wedge-powder) (film recorded)

Untreated		Treated with glycerol		Heated to 600°C	
I	d	I	d	I	d
vvw	5.04			vvw	9.83
ms	4.48				
s(sp)	4.25				
vvw(sp)	4.06				
vw(sp)	3.67				
vvw	3.54				
vs(sp)	3.34				
s(sp)	3.23				
vw(sp)	2.99				
vvw	2.76				
m	2.61				
ms	2.47				
w	2.28				
vw	2.24				
m	2.13				
w(sp)	1.98				
s(sp)	1.82				
m(sp)	1.67				
s	1.54				
vvw	1.51				
vvw	1.46				
s(sp)	1.37				

No change with glycerol treatment

same as untreated

CLAY FROM OLD BEACH ROAD (20)

Table 11 - continued

Oriented Aggregates (film recorded)			
Untreated		Treated with glycerol	
I	d	I	d
s(di. band)	22.61	diffuse band	27.78
vvw	14.23	vvw(di)	17.64
mw(di)	10.95	vw(band)	14.00
m	9.92	m	9.92
vvw	9.29	mw	9.29
mw	7.61		
vw	7.12	mw	7.12
mw	5.00	w	4.97
vvw(di)	4.79	vvw(di)	4.75
vvw(di)	4.47	vvw	4.47
m(sp)	4.27	m	4.27
vvw(di)	3.73	vvw	3.70
vw(di)	3.53	vw(band)	3.48
s	3.36	s	3.36
di.band	3.21	vvw	3.22
mw	3.02	vvw	3.09

Key to abbreviations - same as Table 2

Minerals Identified

The X-ray photographs of the oriented aggregates were taken first with the smaller (3.0 cm.) camera. The interpretation of the lines was complicated due to the presence of some irrational reflections in the photographs. Such reflection may be due to random interstratification of the 'mixed layer' minerals. However a chloritic mineral was also suspected in the clay. The less than two micron clay suspension was treated, with warm dilute HCl, in order to prove the presence of chlorite. The acid treatment gave no change in the reflections of the original (untreated) aggregate pattern. There-fore the irrational interplanar spacings were attributed to the presence of mixed layer minerals.

The larger camera of radius 5.73 cm. was used to establish the presence of higher spacings. The clay gave a non-integral series of basal reflections. These could be explained on the basis of the theory of Henricks and Teller (1942), as due to the random interstratification of different hydrates with different spacings. The recognition of the irrational basal spacings was based on the X-ray data interpreted

by means of the diagrams of Brown and MacEwan (1951). Such diagrams were also used to calculate the ratio of illite-montmorillonite layers. The X-ray patterns (oriented aggregate) of the clay were characterised by the lines at 22.61 Å, 10.95 Å and 3.21 Å which upon glycerol treatment shifted to 27.78 Å, 14.00 Å and 3.47Å respectively. These non-integral reflections were due to a random interstratification of 3 : 2 layers of illite and montmorillonite, which belong to the type of 'mixed layer' minerals. The X-ray data was also compared with 'Mixed layer' minerals present in the bentonite beds from Kinnekull, Sweden (Bystrom 1954). A line at 22.61 Å could be also explained by the presence of a mixed layer mineral of ordered stacking in the ratio of 1 : 1 layers of illite and montmorillonite. This ordered structure of illite and montmorillonite was present in very small amount. A reflection at 7.61 Å which upon glycerol treatment shifted to 17.64 Å was due to gypsum. This identification of the mineral gypsum can be explained on the basis of its structure in which layers of water molecules alternate with $CaSO_4$ layers. The replacement of water by organic liquid-glycerol or ethylene glycol causes an indefinite expansion (about 17 Å) in gypsum which will be similar to the expansion of montmorillonite as "interlamellar sorption" (MacEwan 1955). A line at 9.29 Å

was due to talc. Traces of montmorillonoid were characterised by the presence of a line at 14.23 Å which upon glycerol treatment shifted to 17.64 Å. The mineral kaolinite was identified by the presence of very weak oriented line at 7.12 Å and a diffuse line at, 3.53 Å. Quartz and feldspar the predominant mineral constituents of the clay were identified by their characteristic reflections in the wedge-powder patterns. A muscovite type mica was identified by the medium lines between 3.2 - 2.8 Å present in the photograph of the 'acid treated' oriented aggregate.

The differential thermal curve of the less than 2 micron fraction showed a low temperature endothermic peak at 100°C followed by another endothermic peak at 530°C which were due to the presence of mixed-layer minerals, mica and montmorillonoid.

The mineral composition of clay (20) as determined above from the detailed X-ray examination and differential thermal analysis is in order of abundance:

quartz (very high), feldspar, mixed-layer minerals of illite and montmorillonite - mostly randomly stacked (3 :2) with a small amount of ordered structure (1 : 1) and muscovite mica

with traces of gypsum, talc, kaolinite and montmorillonoid.

CLAY FROM OLD BEACH ROAD (21)

Minerals Identified

The mineral composition as determined was similar to (20). The clay had more quartz, feldspar and mixed layer minerals - randomly stacked 3 : 2 layers of illite and montmorillonite than clay (20) and mica.

CLAY FROM WEST of the JUNCTION on the OLD BEACH ROAD (22)

Minerals Identified

The mineral composition was found to be the same as (21), quartz, feldspar, mixed-layer minerals and mica

CLAY FROM WEST of the JUNCTION on the OLD BEACH ROAD (23)

Minerals Identified

The X-ray diffraction patterns and differential thermal curves were compared with those of clay samples (20, 21 and 22). The mineral composition was quartz, feldspar, mixed layer minerals and mica.

Clay samples 21, 22 and 23 had similar random interstratification of 3 : 2 layers of illite and montmorillonite and belong to the same structural type.

CLAY SAMPLE FROM ROKEBY (27)

Minerals Identified

The whole samples wedge-powder pattern had little indication of any clay minerals present. However the oriented aggregate revealed the presence of quartz, montmorillonoid, kaolinite and mixed layer minerals (Same as 20, 21, 22 and 23).

CLAY SAMPLE FROM ROKEBY (28)

Minerals Identified

The minerals identified in the diffraction patterns were the same as (27), quartz, montmorillonoid, kaolinite and mixed layer minerals (less than clay 27).

TABLE 12.

SUMMARY OF MINERAL COMPOSITION OF THE CLAYS, AS DETERMINED BY X-RAY AND D.T.A. METHODS

Sample No.	Locality	Abnormal montmorillonite	quartz	kaolinite	illite	feldspar	goethite	gibbsite	metahalloysite	calcite	chlorite	haematite	organic matter	muscovite	mixed layer minerals Illite:Montmorillonite (3:2)
1	Glenora	40	30	20	5-10	traces									
1A	"	60	20	5	5		traces	5							
3	Plenty	60	20			traces			10						
16	Macquarie Plains	60	25	5	traces	5									
2	New Norfolk	10	70	5	5	10									
4	Claremont	10	50	40						traces					
5	Cornelian Bay	40	30	25	traces	5									
6	Lawrenny		50	40	5						traces				
7	"	traces	50	40	traces										
8	Fentonbury	20	35	40	5										
9	Dunrobin			60			5	30				5			
12	Kenmere			85			traces	5				10			
10	Sandy Bay	60	20	10	5	traces				1-5					
11	" "	55-60	25-30	10-15	5	traces				traces			present		
13	Ouse	(?) or mixed layer mineral	50	30	5	5									
14	Dunalley	10, montmorillonite or swelling chlorite	40	45	5										
15	Mangalore	40	15-20	40											
18	"	present	Abundant (above 70%)	20						traces					
19	One Tree Point	60	25-30	5-10	5	traces									
17	Launceston		50	45	5										
25	"	less than 5	50	40					1-2				5		
26	"	" " 5	60	35	1-5				1-2						
24	Cressy	5	60	35	5										
20	Old Beach	traces	very high (above 70%)	traces	traces	5							present		
21	" "		"		"	5							Present		5-10 (and traces of talc & gypsum)
22	" "		"			5							"		5-10
23	" "		"			5							"		5-10
27	Roache's Beach	traces	"	traces											5-10
28	" "	"	"	"											5-10

CORRELATION OF LOWER DEHYDRATION REACTIONS IN ABNORMAL MONTMORILLONITES

The differential thermal analysis in no case indicated the presence of a normal type of montmorillonite for they all showed a prominent endothermic peak at about 550°C. The endothermic peak corresponding to the final break down of the lattice of montmorillonite, which is almost invariably present, was absent in these clays and those rich in abnormal montmorillonite did not bear any relation to the mixed-layer minerals. This anomaly is believed to be due to structural differences, which could not be revealed by the X-ray examination.

Effect of Replacement of Al^{3+} by Fe^{3+} in Octahedral Sheet

It is known that normal montmorillonites, in which relatively small amounts of iron and magnesium have replaced aluminium, show an endothermic peak at about 700°C (Grim 1953). This decomposition is mainly due to the loss of OH groups and this dehydration temperature may vary with the amount and type of substitution of Al^{3+} by Fe^{3+} and/or by Mg^{2+}. This temperature is higher than the corresponding dehydration temperature for illites, which is between 550° and 600°C.

As pointed out earlier in the chapter montronite gives its main dehydroxylation peak at 550° to 600°C. But it has been established that the presence of Fe alone does not lower the peak temperature of an iron - rich montmorillonite (Sudo and Ota 1952) and the clays under investigation did not contain nontronite and had a low iron content.

Effect of Tetrahedral Replacement of Si^{4+} by Al^{3+}

In order to explain or correlate the lower endothermic peak in the 550°C region which is invariably present in abnormal montmorillonites, it is referred to illites which have their main endothermic peak at about 550° - 600°C and owe the silicate-layer charge to a high tetrahedral substitution of Al^{+++} for Si^{++++}. But this explanation of high substitution for lower temperature of dehydroxylation for illites could not account for an illite clay from Ballater (Mackenzie, Walker and Hart 1949) which had a higher dehydroxylation temperature. Moreover Earley et al (1953) found no direct correlation between the variations of the main endothermic peak (650° - 715°C) and constitution over the limited compositional range from

$$(Al_{3.13}\ Fe^{+++}_{0.61}\ Mg_{0.31})\ (Si_{7.31}\ Al_{0.69})\ O_{20}\ (OH)_4$$

to $$(Al_{2.64}\ Fe^{+++}_{0.12}\ Mg_{1.42})\ (Si_{7.90}\ Al_{0.10})\ O_{20}\ (OH)_4$$

so that they related the variations to differences in crystal size. The results are in agreement with the experimental results of Kelley, et al (1936), Kulp and Trites (1951), where the temperatures of thermal reactions of layer silicates containing hydroxyl groups are decreased by decreasing particle size, but this may not be a complete explanation. For example, electronic micrographs of the sodium bentonite (Wyoming) show high crystal organisation and a large proportion of smaller particle size. A few more similar examples are also known (Greene-Kelley 1957). However none of these arguments seems to be an appropriate explanantion.

Laboratory Experiments for Preparing Abnormal Montmorillonite

There are laboratory experiments to indicate that a normal montmorillonite can be converted to an abnormal one. Grim and Bradley (1948), Hill (1953) and Jonas (1955) prepared rehydrated forms of some heated (800°C) clay minerals (Montmorillonite) by allowing them to stand for long periods of time at atmospheric pressure and temperature, or by

rehydrating the product in steam. The rehydrated montmorillonites showed two dehydroxylization reactions, one peak at 550°C and the other at 700°C. These observations led Grim and Bradley (1948) to conclude that the structure of the rehydroxylated material was different from that of the original clay mineral. Such rehdrated minerals have some lattice defects. These laboratory experiments support the belief that a normal montmorillonite can be modified to an abnormal type by an order-disorder transformation, and that intermediates can be produced by, what is tentatively believed to be random interstratification of ordered and disordered structures (Cole and Hosking 1957).

Such anhydrides, which develop with the high temperature reactions must be independent of the occurrence of natural abnormal montmorillonites (Tertiary lacustrine clays). It is almost certain that rehydrated forms of montmorillonites do exist in nature and they formed as a result of some process other than rehydroxylization of the anhydride product. The probable mechanism is described at the end of this chapter.

Effect due to Mixed-layer Minerals.

Some pure dioctahedral montmorillonites give low endothermic peaks, but they appear to be of the mixed-layer

type (Grim 1953, Grim and Johns 1954, and Keller 1953). The clay samples found rich in abnormal montmorillonites did not correspond to the mixed-layer minerals.

Conclusions

Kerr, Kulp and Hamilton (1949) have considered that in montmorillonite structure the hydroxyl groups are attached only to certain cation positions. If substitution of replaceable ions was random in the octahedral sheet, then a highly substituted montmorillonite might show a high temperature endothermic reaction for OH loss, because the hydroxyls would still be essentially bound to aluminum atoms, on the other hand a slightly substituted montmorillonite shows a lower temperature endothermic reaction.

Such an order - disorder (Cole and Hosking 1957) transformation of minerals takes place in certain stages of the weathering sequences of layer silicates (Nagelschmidt 1944, Jackson et al 1952) as shown by:

mica ⟷ illite ⟷ intermediates ⟷ abnormal montmorillonite

where an illite transforms to an abnormal montmorillonite, but the hydroxyl bondings within the layers will remain of the

illite type. This could be an explanation for a lower temperature endothermic reaction in the abnormal montmorillonites, which is in harmony qualitatively with the highly disordered structures (as compared to the Wyoming bentonite which has an ordered structure and crystal organisation and is characterised by diagnostic higher endothermic peak at 700°C).

The author feels that such large variations by a deviation of 150°C in the dehydroxylization curves of abnormal montmorillonites can be related to structural changes brought about by certain modifications in their geometrical atacking. It may be due to the degradation of illite which may be brought about by some chemical or physical processes, such as the oxidation of iron in the octahedral sheets which probably gives rise to a disorder structure. This suggestion is very strongly supported by the decrease in intensity and broadening of the basal reflections (001) of abnormal montmorillonites, in their oriented aggregate diffraction patterns. The oxidation of iron will bring a change in the net change of the lattice, thereby weakening the forces between the sheets so that water or other solutions may remove potassium ions from illite. This type of phenomenon may give rise to an expanding-type of clay mineral - abnormal montmorillonite - which has a disordef structure.

PHYSICAL PROPERTIES OF CLAYS

To assess the industrial value of any clay it is important to study its plasticity, drying and firing shrinkage, colour after firing and fusion point or refractoriness.

PREPARATION OF TEST PIECES

About 50 ozs. of a representative sample of each clay were mixed with sufficient water to give plasticity. The tempered clay was hand-moulded into briquettes of size $4\frac{1}{2}$" x $2\frac{1}{4}$" x $1\frac{1}{2}$". Six test pieces were prepared for each clay. The briquettes were cut longitudionally into specimens of size $4\frac{1}{2}$" x $1\frac{1}{8}$" x $\frac{3}{4}$".

The test pieces were weighed and marked for subsequent shrinkage determination. They were dried at room temperature, but some of them were covered with a damp cloth and dried slowly (clays which had a higher proportion of water for moulding). The dry weight and the shrinkage of specimens were determined.

PLASTICITY

No direct method of measuring plasticity was

attempted, but the moulding properties were observed while preparing small bricks.

FIRING OF BRIQUETTES

The colour of products of clays after firing is of practical interest. The test pieces or the briquettes were dried in an oven at 110°C. Then they were fired in an electric muffle (in oxidizing atmosphere) over a temperature range of 850° ÷ 1100°C, followed by a soaking period of one hour.

Total linear shrinkage, firing colour and water were determined and are given in tabular form.

CALCULATIONS FOR PROPERTIES AND CONDITIONS OF THE SPECIMENS BURNT OVER THE TEMPERATURE RANGE 850° - 1100°C

1. Total weight loss after firing = $\frac{\text{Raw wt. - Fired wt.}}{\text{Raw wt.}} \times 100$

2. Firing shrinkage = Total linear shrinkage - linear shrinkage after drying

3. Water absorption = $\frac{\text{wt. after boiling - fired wt.}}{\text{fired wt.}} \times 100$

4. % water added = $\frac{\text{wt. of water}}{\text{wt. of air - dry clay}} \times 100$

Properties and Conditions of the specimens burnt over the temperature range 850° - 1100°C

Sample No.	Briquettes No.	water added	Raw weight gms.	Dry weight gms.	Dry shrinkage %	Fired weight gms.	Total weight loss on firing %	Total shrinkage %	Weight after boiling gms.	Water absorption %	Firing temp. °C	Colour after firing	Hardness	Remarks
1	a	46	185	123	14.2	113	38.9	15.4	133	17.7	850	Buff	Hard	No cracks or deformation
	b		181	120	14.0	110.5	38.9	15.0	131	17.6	900	"	"	"
	c		184	122	13.4	112	39.1	15.6	130	16.1	950	"	"	"
	d		185	123	13.4	113	38.9	16.6	128	13.3	1000	"	"	"
	e		186	123.5	13.8	113	39.2	20.5	120	6.2	1050	"	very hard	"
	f		186	124	13.6	113.5	39.0	21.3	115	1.3	1100	light red	"	"
1A	a	40	200	138	12.8	128	36	13.3	155	21.1	850	red brown	Hard	"
	b		195	134	12.6	122	37.4	15.4	144	18.0	900	Red	"	"
	c		202	140	12.6	127	37.1	17.6	144	13.4	950	"	"	Several cracks, formed during drying. No deformation.
	d		198	137	12.6	124	37.4	20.0	134	8.1	1000	"	"	Few small cracks, during dyring. No deformation
	e		196	135	12.4	122.5	37.5	21.2	128	4.5	1050	Red brown	very hard	
	f		203	141	12.5	127	37.4	21.5	131	3.2	1100	"	"	Cracks across edges. No deformation.

Properties and conditions of the specimens burnt over the temperature range 850° - 1100°C

Sample No.	Briquettes No.	water added %	Raw weight gms.	Dry weight gms.	Dry shrinkage %	Fired weight gms.	Total weight loss on firing %	Total shrinkage %	Weight after boiling gms.	Water absorption %	Firing temp. °C	Colour after firing	Hardness	Remarks
3	a	32	189	136	7.6	128.5	732	7.2	164	27.6	850	Buff	Soft	No cracks or deformation
	b		210	151	7.7	140.5	33.1	7.9	181	28.8	900	"	"	"
	c		200	144	7.6	134	33	8.5	170	26.9	950	"	fairly soft	"
	d		201	144	7.6	133.5	33.6	9.2	168	25.8	1000	"	"	"
	e		197	141	7.5	131	33.5	11.1	160	22.1	1050	"	"	"
	f		200	143	7.6	132.5	33.8	12.2	158	19.2	1100	Pink	Hard	"
16	a	32	190	137	4.7	130	31.6	4.6	175	34.6	850	orange brown	very soft	"
	b		203.5	147	4.7	138	32.2	5.4	184	33.3	900	"	"	"
	c		194	140	4.9	131	32.5	6.4	173	32.1	950	"	"	"
	d		205	147	5.0	138	32.7	7.0	181	31.2	1000	"	"	"
	e		196	141	5.0	132	32.7	7.9	170	28.8	1050	"	"	"
	f		205	148	4.7	139	32.2	8.9	175	25.9	1100	red brown	fairly soft	"

Properties and conditions of the specimens burnt over the temperature range 850° - 1100°C

Sample No.	Briquettes No.	water added %	Raw weight gms.	Dry weight gms.	Dry shrinkage %	Fired weight gms.	Total weight loss on firing %	Total shrinkage %	weight after boiling gms.	water absorption %	Firing temp. °C	Colour after firing	Hardness	Remarks
2	a	*	98	92	0	88	10.2	0	104	18.2	850	orange brown	soft	No cracks or deformation
	b		99	93	0	88.5	10.6	0	106	19.8	900	"	"	"
	c		99	93	0	88.5	10.6	0	106	19.8	950	"	"	"
	d		98	91	0	86	12.2	0	104	20.9	1000	"	"	"
	e		99	93	0	88	11.1	0	104	18.2	1050	brown	"	"
	f		98	93	0	88	10.2	1.5	103	17.1	1100	dark red	fairly soft	"
4	a	30	201	150	9.4	137.5	31.6	10.0	160	16.4	850	pinky-cream	hard	"
	b		206	153	9.7	140	32.0	11.1	162	15.7	900	"	"	"
	c		208	155	9.2	141.5	32.0	10.4	164	15.9	950	"	"	"
	d		200	149	9.0	135	32.5	10.8	156	15.6	1000	"	"	"
	e		204	152	9.4	138	32.4	12.6	154	11.6	1050	"	very hard	"
	f		205	153	9.2	138	32.7	13.0	152	10.1	1100	cream	"	"

* water added 6% only. Very difficult for hand-moulding because of lack of plasticity. Suitable for dry-pressing.

Properties and conditions of the specimens burnt over the temperature range 850° - 1100°C

Sample No.	Briquettes No.	water added %	Raw weight gms.	Dry weight gms.	Dry shrinkage %	Fired weight gms.	Total weight loss on firing %	Total shrinkage %	Weight after boiling gms.	Water absorption %	Firing temp. °C	Colour after Firing	Hardness	Remarks
5	a	39	183	126	10.0	119	35.0	9.8	148	24.4	850	white	fairly hard	No cracks or deformation
	b		181	125	10.3	117	35.4	10.4	146	24.8	900	"	"	"
	c		181	125	10.2	117	35.4	10.7	146	24.8	950	"	hard	"
	d		183	127	10.0	118	35.5	10.8	147	24.6	1000	"	"	"
	e		188	130	10.3	121	35.6	13.0	145	19.8	1050	"	"	"
	f		184	128	10.2	119	35.3	14.2	139	16.8	1100	cream	very hard	"
6	a	32	204	151	9.5	140	31.4	9.8	166	18.6	850	white	fairly hard	"
	b		202.5	149.5	9.0	137.5	32.1	9.3	163	18.5	900	"	"	"
	c		199	147	9.0	135	32.2	9.3	160	18.5	950	"	hard	"
	d		209	155	9.0	142	32.1	9.8	168	18.3	1000	"	"	"
	e		203.5	151	8.8	138	32.2	10.5	161	16.7	1050	"	"	"
	f		196	144.5	8.8	132	32.7	11.4	150	13.6	1100	"	"	"

Properties and conditions of the specimens burnt over the temperature range 850° - 1100°C

Sample No.	Briquettes No.	water added %	Raw weight gms.	Dry weight gms.	Dry shrinkage %	Fired weight gms.	Total weight loss on boiling %	Total shrinkage %	Weight after boiling gms.	Water absorption %	Firing temp. °C	Colour after firing	Hardness	Remarks
7	a	32	196	145.5	9.0	133	32.1	9.4	157	18.0	850	white	hard	No cracks or deformation
	b		197.5	146	8.6	135	31.6	8.6	159	17.8	900	"	"	"
	c		201	149	8.2	136	32.3	8.9	160	17.6	950	"	"	"
	d		201	149	8.7	136	32.3	10.0	159	16.9	1000	"	very hard	"
	e		203	151	8.9	139	31.5	10.7	161	15.8	1050	"	"	"
	f		202	149.5	8.4	136	32.7	13.0	149	9.6	1100	"2	"	"
9	a	38	201.5	142	4.8	122	39.5	8.1	169	38.5	850	Red	very soft	Surface crazing. No deformation
	b		208	146	4.8	127	38.9	7.2	177	39.4	900	Red	"	Further crazing No deformation
	c		204	144	4.8	123	39.7	9.1	170	38.2	950	brown red	"	crazing and some cracks No deformation
	d		207	145.5	4.7	123	40.6	9.5	170	38.2	1000	"	"	Much crazing. No deformation
	e		205	145	4.8	123	40.0	11.9	164	33.3	1050	"	"	"
	f		208	147	4.8	124	40.4	15.7	156	25.8	1100	"	"	crazing and some cracks No deformation

Sample No. 8 (Fentonbury) - was not studied, because of small quantity.

Properties and conditions of the specimens burnt over the temperature range 850° - 1100°C

Sample No.	Briquettes No.	water added %	Raw weight gms.	Dry weight gms	Dry shrinkage %	Fired weight gms.	Total weight loss on firing %	Total shrinkage %	Weight after boiling gms.	Water absorption %	Firing temp. °C	Colour after firing	Hardness	Remarks
	a		197	143.5	8.9	119	39.6	12.2	152	27.7	850	orange red	hard	Surface crazing. Cream patch warped.
	b		193	140	9.1	115	40.4	13.6	146	27.0	900	"	"	as for b.
	c		196	143	8.6	118	39.8	12.6	150	27.1	950	"	"	"
12	d	40	196	143	8.6	118	39.8	13.0	148	25.4	1000	"	"	Surface cracking. Cream patch. No deformation
	e		193	140	9.0	115	40.4	14.5	142	23.5	1050	light brown	"	Much cracking. Dark patch. Overburnt. Warped.
	f		193	140	9.0	115	40.4	17.6	132	14.8	1100	"	"	very badly cracked warped.
	a		185.5	127	13.6	117	36.9	14.4	139	18.8	850	light orange brown	hard	Few very small cracks No deformation
	b		184	126	14.0	117	36.4	14.4	139	18.8	900	"	"	as for b
10	c	37.8	186	128	13.9	116	37.6	15.1	136	17.2	950	orange	"	"
	d		188	129	13.7	117.5	37.5	16.2	134	14.0	1000	light orange brown	"	"
	e		190.5	131	13.5	119	37.5	16.5	134	12.6	1050	"	"	"
	f		190	130	13.6	118	37.9	17.0	132	11.9	1100	light red	"	"

Properties and conditions of the specimens burnt over the temperature range 850° - 1100°C

Sample No.	Briquettes No.	water added %	Raw weight gms.	Dry weight gms.	Dry shrinkage %	Fired weight gms.	Total weight loss on firing %	Total shrinkage %	Weight after boiling gms.	Water absorption %	Firing temp. °C	Colour after firing	Hardness	Remarks
	a		193	146.5	9.8	122	36.8	10.7	153	25.4	850	light brown	fairly hard	No cracks or deformation Dark Patch, due to carbonaceous material
	b		192	146	9.5	120	37.5	10.4	149	24.2	900	"	"	As above. Less dark patch
11	c	32	194	148	9.8	121	37.6	10.9	151	24.8	950	"	hard	Several cracks. No deformation. Less patch
	d		193	146.5	9.6	120	37.8	10.8	148	23.3	1000	light orgage brown	"	Crack along sides. No deformation
	e		194	148	9.7	121	37.6	10.7	150	24.0	1050	light brown	"	Cracks and Bloating Purplish patch
	f		189	144	9.6	118	37.6	10.7	147	24.6	1100	Red	"	Cracked and Bloated Purlish patch
	a		219	184	6.8	171	21.9	6.6	196	14.6	850	Pink	"	No cracks or deformation
	b		213	178	7.4	164	23.0	7.1	189	15.2	900	"	"	"
13	c	21	215	180	7.6	167	22.3	7.6	192	15.0	950	"	"	"
	d		217	181.5	7.4	168	22.6	7.6	193	14.9	1000	"	"	"
	e		219	184	6.8	170	22.4	7.5	194	14.1	1050	"	"	"
	f		216	181	6.9	168	22.2	8.3	189	12.5	1100	darker red	"	"

Properties and conditions of the specimens burnt over the temperature range 850° - 1100°C

Sample No.	Briquettes No.	water added %	Raw weight gms.	Dry weight gms.	Dry shrinkage %	Fired weight gms.	Total weight loss on firing %	Total shrinkage	Weight after boiling %	Water absorption %	Firing temp. °C	Colour after firing	Hardness	Remarks
14	a	26	210	163	8.3	150	28.6	8.7	174	16.0	850	pinkish white	hard	No cracks or deformation
	b		206	160	8.1	146	29.1	9.1	170	16.4	900	"	"	"
	c		208	162	8.1	148	28.8	9.4	173	16.9	950	"	"	"
	d		205	159.5	7.8	146	28.8	9.1	171	17.1	1000	"	"	"
	e		205	159.5	7.9	146	28.8	9.8	168	15.1	1050	"	"	"
	f		209	163.7	7.9	148	29.2	12.8	162	9.5	1100	Cream	"	"
15	a	34	190	133	12.6	122	35.8	13.0	141	15.6	850	pinkish	"	"
	b		192	135	12.3	123	35.9	13.2	141	14.6	900	"	"	"
	c		192	136	12.7	124	35.4	14.2	141	13.7	950	"	"	"
	d		192	135	12.6	123	35.9	14.2	140	13.8	1000	"	"	"
	e		189	134	12.7	122	35.5	15.6	139	13.9	1050	cream	very hard	"
	f		196	138	12.3	126	35.7	17.1	133	5.6	1100	pinky cream	"	"

Properties and conditions of the specimens burnt over the temperature range 850° - 1100°C

Sample No.	Briquettes No.	water added %	Raw weight gms.	Dry weight gms.	Dry shrinkage %	Fired weight gms.	Total weight loss on firing %	Total shrinkage %	Weight after boiling gsm	Water absorption %	Firing temp. °C	Colour after firing	Hardness	Remarks
18	a	27.8	203	155	9.5	141	30.5	9.4	167	18.4	850	cream	hard	No cracks or deformation
	b		201	154	9.6	138	31.3	9.9	164	18.8	900	"	"	"
	c		202	154.5	9.5	138.5	31.4	9.9	165	19.1	950	"	"	"
	d		203	155	9.5	139	31.5	10.0	165	18.7	1000	"	very Hard	"
	e		203	155	9.6	139	31.5	10.7	164	18.0	1050	"	"	"
	f		203	155	9.5	139	31.5	11.1	163	17.3	1100	fawn	"	"
19	a	34.2	185	130	9.5	122	34.1	9.5	155.5	27.5	850	Buff	fairly Hard	"
	b		192	135	9.3	127	33.9	9.4	161	26.8	900	"	"	"
	c		187	132	9.5	124	33.7	10.6	156	25.8	950	"	hard	"
	d		187	132	9.6	124	33.7	11.0	155	25.0	1000	"	"	"
	e		188	133	9.5	125	33.5	12.9	156	24.8	1050	light brown	"	"
	f		187	132	9.6	123	34.2	14.3	144	17.1	1100	red brown	"	"

Properties and conditions of the specimens burnt over the temperature range 850° - 1100°C

Sample No.	Briquettes No.	water added %	Raw weight gms.	Dry weight gms.	Dry shrinkage %	Fired weight gms.	Total weight loss on firing %	Total shrinkage %	Weight after boiling gms.	Water absorption %	Firing temp. °C	Colour after firing	Hardness	Remarks
	a		184.5	125	11.9	116	37.1	12.3	141	21.6	850	white	hard	No cracks or deformation
	b		183.5	125	11.9	114	37.9	12.7	140	22.8	900	"	"	"
17	c	44.6	182	125	11.8	115	36.8	13.0	140	21.7	950	"	"	"
	d		185	126	11.9	116	37.3	13.2	141	21.6	1000	"	very hard	"
	e		187	128	11.8	117	37.4	13.4	142	21.4	1050	"	"	"
	f		182	124	11.7	113	37.9	14.6	134	18.6	1100	"	"	"
	a		210	158	8.2	144	31.4	8.3	171	18.8	850	whitish	hard	"
	b		199	149	8.4	135	32.2	8.9	160	18.5	900	"	"	"
25	c	32	200	150	8.1	136	32.0	8.9	161	18.4	950	"	"	"
	d		206	154	8.2	140	32.0	9.2	164	17.1	1000	"	very hard	"
	e		202	152	7.9	137	32.2	10.0	159	16.1	1050	"	"	"
	f		202	151	7.4	137	32.2	11.6	153	11.7	1100	"	"	"

Properties and conditions of the specimens burnt over the temperature range 850° - 1100°C

Sample No.	Briquettes No.	water added %	Raw weight gms	Dry weight gms.	Dry shrinkage %	Fired weight gms.	Total weight loss on firing %	Total shrinkage %	Weight after boiling gms.	Water absorption %	Firing temp. °C	Colour after firing	Hardness	Remarks
26	a	26	206	163	8.0	155	24.8	7.7	180	16.1	850	pink	fairly hard	No cracks or deformation
	b		210	166	8.0	157	25.2	7.9	183	16.6	900	"	"	"
	c		207	164	8.0	154	25.6	8.2	179	16.2	950	pale pink	hard	"
	d		217	173	7.9	164	24.4	8.1	190	15.9	1000	"	"	"
	e		208	164	8.1	155	25.5	8.8	179	15.5	1050	"	"	"
	f		214	169	8.0	160	25.2	9.5	182	13.8	1100	buff	"	"
24	a	30	201	150	10.2	140	30.3	10.1	163	16.4	850	pink	fairly hard	"
	b		199	148	10.1	136.5	31.4	10.3	158	15.8	900	"	hard	"
	c		204	152	10.1	140	31.4	10.5	163	16.4	950	"	"	"
	d		196	146	10.2	134	31.6	10.8	155	15.7	1000	"	"	"
	e		206	155	10.2	142	31.1	11.4	163	14.8	1050	"	"	"
	f		199	149	9.6	137	31.2	12.2	153	11.7	1100	"	"	"

Properties and conditions of the specimens burnt over the temperature range 850° - 1100°C

Sample No.	Briquettes No.	water added %	Raw weight gms.	Dry weight gms.	Dry shrinkage %	Fired weight gms.	Total weight loss on firing %	Total shrinkage %	Weight after boiling gms.	Water absorption %	Firing temp. °C	Colour after firing	Hardness	Remarks
	a		204	158	10.2	151	26.0	9.9	172	13.9	850	light brown	fairly hard	No Cracks or deformation
	b		202	157	10.3	148	26.7	10.2	167	12.8	900	orange	hard	"
20	c	24.4	204	159	10.4	149	27.0	11.0	166	11.4	950	"	"	"
	d		205	161	10.2	151	26.3	11.1	167	10.6	1000	"	"	"
	e		202.5	157	10.4	148	26.9	12.9	160	8.1	1050	light brown	very hard	"
	f		202	157	10.3	148	26.7	14.6	153	3.4	1100	red	"	"
	a		204	155.5	9.7	150	26.5	9.2	173	15.3	850	light brown	fairly hard	"
	b		207	161	9.2	152	26.6	8.9	174	14.5	900	orange	hard	"
21	c	26.6	210	163	9.2	153	27.1	10.0	171	11.8	950	"	"	"
	d		210	162	9.2	152	27.6	10.2	169	11.2	1000	"	"	"
	e		210	162.5	9.4	153	27.1	12.4	165	7.8	1050	light brown	very hard	"
	f		209	162.5	9.4	152	27.3	14.8	158	3.9	1100	red	"	"

Properties and conditions of the specimens burnt over the temperature range 850° - 1100°C

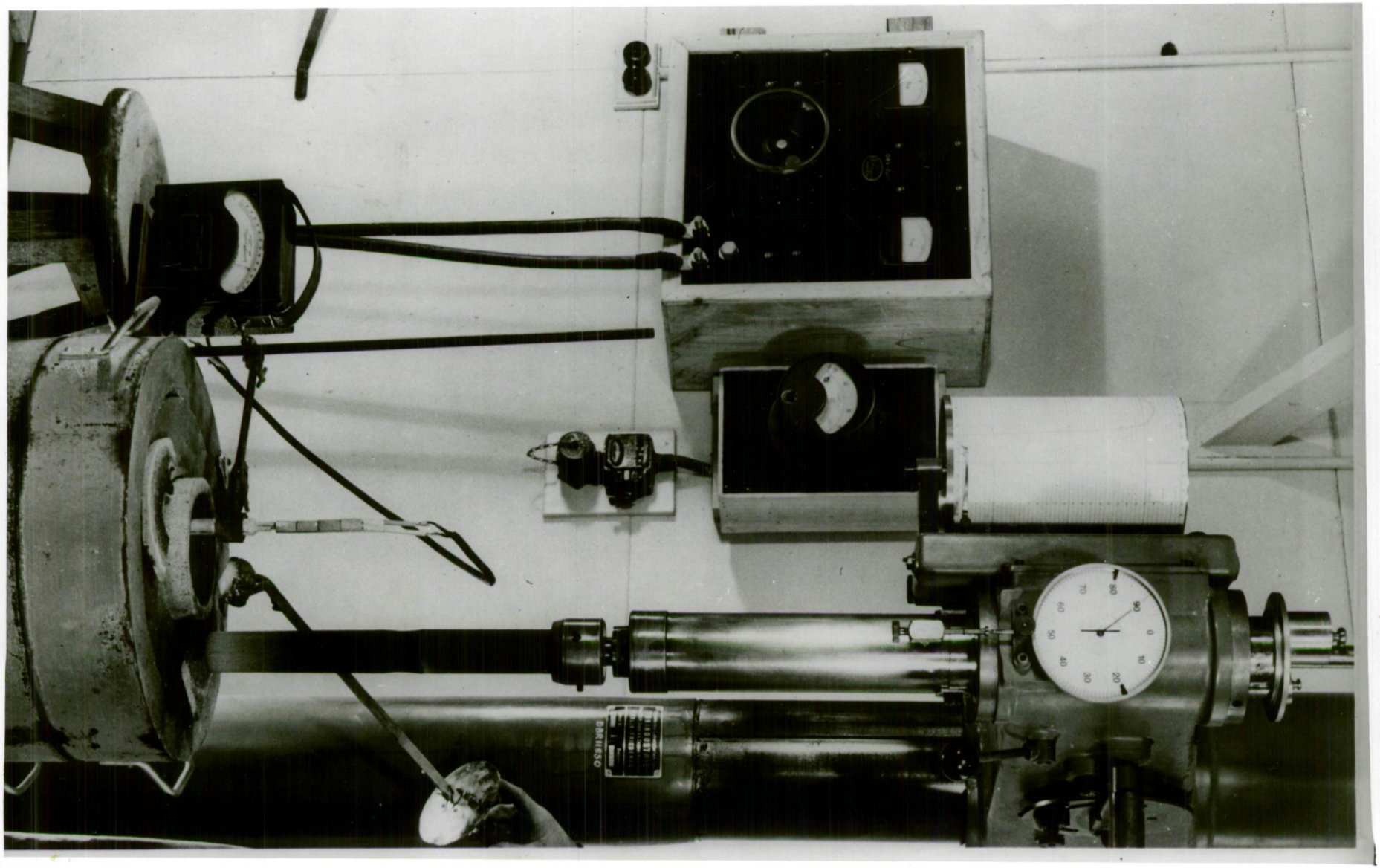
Sample No.	Briquettes No.	water added %	Raw weight gms.	Dry weight gms.	Dry shrinkage %	Fired weight gms.	Total weight loss on firing %	Total shrinkage %	Weight after boiling gms.	Water absorption %	Firing temp. °C	Colour after firing	Hardness	Remarks
22	a	30	198	147	12.3	138	30.3	12.3	156	13.0	850	brown	hard	No cracks or deformation
	b		198	147	12.4	138	30.3	12.6	152.5	10.5	900	orange red	hard	Long fine cracks No deformation
	c		198	148	12.6	138	30.3	13.6	150.7	8.7	950	"	"	"
	d		198	147	12.3	138	30.3	13.4	148	7.2	1000	"	"	More and larger cracks Bloating beginning
	e		198	148	11.9	138	30.3	-	152	10.1	1050	brown	"	Badley cracked and bloated
	f		194	145	12.0	135	30.4	-	150	11.1	1100	red brown	"	"
23	a	24	201	154	10.3	146	27.4	10.3	164	12.3	850	brown	hard	No cracks or deformation
	b		207	160	10.6	150	27.5	10.9	167	11.3	900	light brown	"	"
	c		205	159	10.6	148	27.8	11.1	166	12.2	950	orange brown	"	"
	d		204	157	10.7	147	27.9	11.5	163	10.9	1000	orange red	"	Few fine cracks. No deformation
	e		203	157	10.7	147	27.6	12.1	161	9.5	1050	"	"	"
	f		203	157	10.5	147.5	27.3	14.0	157	6.4	1100	red	very hard	Many long cracks No deformation

Properties and conditions of the specimens burnt over the temperature range 850° - 1100°C

Sample No.	Briquettes No.	water added %	Raw weight gms.	Dry weight gms.	Dry shrinkage %	Fired weight gms.	Total weight loss on firing %	Total shrinkage %	Weight after boiling gms.	Water absorption %	Firing temp. °C	Colour after firing	Hardness	Remarks
27	a	30	192	144	12.3	136	29.2	12.3	155	14.0	850	Brown	Hard	No cracks or deformation
	b		194	145	12.3	138	28.9	12.5	156	13.0	900	"	"	Few small fine cracks. No deformation
	c		195	147	12.0	139	28.7	12.3	157	13.0	950	light brown	"	as for b.
	d		199	149	12.2	141	29.1	12.9	158	12.1	1000	"	"	long fine cracks
	e		199	149	12.0	141	29.1	13.4	155	9.9	1050	"	"	No deformation long cracks
	f		202	153	12.0	144	28.7	14.4	158	9.7	1100	red brown	"	As for e
28	a	31	210	166	8.3	159	24.3	7.8	187	17.6	850	red brown	fairly soft	No cracks or deformation White specks.
	b		205	160	8.7	153	25.4	7.2	180	17.6	900	"	"	"
	c		206	164	8.1	156	24.3	7.9	182	16.7	950	red	"	"
	d		212	168	8.2	160	24.5	8.0	186	16.3	1000	"	"	"
	e		210	166	8.4	158	24.8	8.2	187	18.4	1050	"	"	"
	f		212	168	8.0	160	24.5	8.0	187	16.9	1100	"	"	"

DEFORMATION UNDER LOAD TEST APPARATUS

PLATE IB



FIRING CHARACTERISTICS OF THE CLAYS

Deformation under load test

In order to have more information on the firing properties of clays, the simplest way of evaluating them is by means of the deformation under load test.

The test was carried out on two small dry-pressed samples of size 1" by 1" and the equipment used is described in the D.I.N. (German standard). The equipment consists essentially of a carbon granule resistance furnace (Plate IB) operated through a step transformer and a vertical column through which the load is applied and having a pen and drum connected to produce a time deformation curve. A dial gauge is attached to the load column, independently of the pen and drum mechanism for determining accurate readings of expansion or shrinkage of the 1" x 1" test pieces. Temperatures up to 1250°C were measured by a chromel-alumel thermocouple sheathed in a mullite tube, and for higher temperatures, when necessary, an optical pyrometer of the disappearing filament type was used. The sample consisting of two 1" cubes was set under a constant load of 25lb/in^2 and the sample was placed upon the end of a carbon rod, which rests vertically on the furnace floor, and is of such a length as to allow the sample to stand at the centre of the furnace. The rise in temperature

was 1250°C per hour and the atmosphere in the furnace was reducing.

Load is applied by a metal ~~carbon~~ column through another carbon rod. The metal column and carbon rod which are rigidly attached are free to rise and fall as the sample expands or contracts. Such a rise and fall is transmitted to the graph paper on the drum by means of the pen mechanism, which consists of a rack (column) and pinion, the movement to the pen being magnified with a system of pulleys.

The graphs, plotted automatically, were of expansion or contraction against time of the inch cubes and are given in plates (2A-2H). The temperatures at commencement of expansion, maximun expansion and commencement of shrinkage are shown on the plates by the vertical arrows.

Appraisal of Clays from the firing tests

Most of the clays required a large amount of tempering water (30 - 45%) to render them workable for forming by hand-moulding, consequent drying, shrinkage and extrusion troubles could be the result. All the clays containing 35% or more water calculated on the air-dry basis, would need protection

during the initial stages of drying to avoid cracking. Even so, high shrinkage and possible warpage of bricks etc. can be expected. Such clays for extrusion of bricks or pipe manufacturing require the addition of shorter (non-plastic - semi-plastic) clays or grog to reduce the tempering water and consequently to reduce the shrinkage and possibility of cracking during drying. Such clays also would probably show 'S' cracks after drying when extruded as bricks or splits if extruded as pipes. Shortening with other clays or grog could help to overcome the trouble.

The clays from Lawrenny (6 and 7) and Launceston (17 and 25), having kaolinite as the abundant clay mineral, may be useful in the manufacture of whitewares as the clays are white burning over a wide vitrification range and are refractory. The clays rich in abnormal montmorillonite had a very high plasticity, green strength, short vitrification range and high drying and firing shrinkage and burnt orange - red brown.

INTERPRETATION OF THE ENVIRONMENTS OF DEPOSITION FROM THE CLAY MINERAL COMPOSITION

Inferences concerning the environments of a formation can be derived from the occurrence, texture and composition of a representative sample of the rocks or minerals. As environments are responsible for the character of clay minerals, a characteristic clay mineral might be a sequel to every change in an environment. The sensitivity of clay minerals to different environments has been discussed by Ross 1943, Ross and Hendricks 1945, Keller 1946, Millot 1949 and 1952, Dietz and Bradley 1949, Keller and Ting 1950, Grim 1951, Keller 1952, 1953 and 1955, Jackson et al. 1948 and 1952 and Mohr and Van Baren 1954. Their general conclusion is that clay minerals which result from sedimentation may be used in a qualitative way as mineral indicators of the physical and chemical environments during deposition and diagenesis. However, there are insufficient data on the clay mineralogy of recent and ancient sedimenta of known origin and there are many difficulties in conveying full geological information about the origin of different clay minerals and their use as ideal mineral indicators. It is not possible to differentiate between allothogenic and authigenic—

clay minerals in an outcrop. It may be quite incorrect to assume that a clay mineral occurring in a certain outcrop was also formed there. Furthermore, after the initial formation of a clay mineral, it may be altered by the action of ground water, and thereby its nature (regarding composition) and history complicated for a geologist who tries to interpret and reconstruct the environments. It is quite impossible at present to evaluate the relative importance of different geological processes or environments of weathering, sedimentation and diagenesis in the formation of clay minerals.

Despite these shortcomings, some trustworthy information can be derived from the clay minerals which may be excellent indicators of environments because of their sensitivity to slight changes in the composition, temperature and pH of their surroundings (Frederickson 1952) Hence while keeping in mind the limitations and precautions, an attempt has been made to analyse the environmental conditions under which the individual clay minerals formed in the sediments of the Cainozoic Era.

From Table (12) it will be observed that the Cainozoic clays can be classified into five types, on the basis of the presence of the most predominant clay minerals, as follows:

(1) Clays rich in kaolinite from Windermere Beach (4), Lawrenny (6 and 7), Q/MP 105 (13), Dunalley Canal (14), Mangalore (18), Launceston (17, 25 and 26) and Brumby Creek (24).

(2) Clays rich in abnormal montmorillonite from Glenora (1 and 1A), Plenty (3), Cornelian Bay (5), Macquarie Plains (16), New Norfolk (2), Sandy Bay (11 and 10) and One Tree Point, Sandy Bay (19).

(3) Clays characterised by mixed layer minerals of illite and montmorillonite, most randomly stacked by 3 : 2 from Old Beach (20, 21, 22 and 23) and Rokeby (27 and 28)

(4) Clays characterised jointly by kaolinite and abnormal montmorillonite from Fentonbury (8) and Mangalore (15).

(5) Clays predominantly kaolinites with gibbsite from Dunrobin Bridge (9) and Kenmere Hill (12).

ENVIRONMENT OF DEPOSITION

The genesis of clay minerals in the Tasmanian Tertiary lakes is a difficult subject because of the different clay minerals found in them. Environmental conditions possibly favoured the formation of a specific clay mineral, while other

physical and chemical conditions varied. Differences in clay mineral composition might arise if their alteration occurred in response to a particular environment. The environment bringing about the alteration might have prevailed at any stage during erosion and/or deposition. Different clay minerals may have formed as a result of a climatic change trend.

With regard to the environment of deposition, Millot's work (1949) in France suggests that kaolinite is the characteristic mineral of lacustrine environment and one might expect little variation in clay mineral composition, from one lake to another.

Type (1)

Here kaolinite is the abundant clay mineral. The factors conducive to the formation of kaolinite are -

(a) the efficient removal of metal cations (Fe, Ca, Mg, Na and K) other than Al and Si (Ross 1943)

(b) a supply of adequate amount of H^+ ions (Ross 1943)

(c) strong leaching (where precipitation exceeds evaporation), which implies abundant rainfall, permeable rocks (Triassic sediments) and favourable topography.

The parent rocks contributing towards the formation of the clay mineral kaolinite may be Jurassic (?) dolerites, Triassic feldspathic sandstones and Permian sediments. Kaolinite developed in an acidic environment under warm and humid climate, where intense leaching processes prevailed and weathering and oxidizing conditions were rapid. The abundance of rainfall together with $C\theta_2$ and organic acids from decaying plant matter favoured the removal of alkalies and alkaline earths. There was no contemporaneous deposition of any calcareous rocks in the near vicinity of the clays, a condition which is sonsistent with the usual occurrence of kaolinite (Millot 1952). In environments of deposition, kaolinite formation is favoured by an abundance of circulating, "aggressive" acid waters (having a high H^+ concentration) which characterize the continental lacustrine and fluviolacustrine facies (Millot 1952). The genesis of kaolinite is further supported by the presence of Tertiary plant fossils found in the Lower Tertiary Launceston Series. The fossils suggest a warmer and more humid climate during sedimentation than at the present day.

Physical and Chemical factors

The physical and chemical factors in the depositional environment control the formation of a particular clay mineral. The cations common to the clay mineral groups is silicon. The solubility of silica and alumina are functions of pH because alumina is soluble below pH 4 and above pH 9 and the solubility of silica increases linearly with increasing pH. In an acidic environment, the alumina is enriched relative to silica, thereby setting up a high Al : Si ratio, which is found in kaolinite.

These physical and chemical relationships explain that kaolinite formed in Type (1) from the weathering of mafic rock (dolerite) and/or Triassic feldspathic sandstones, where leaching was sufficiently thorough, precipitation exceeded evaporation and the alkali metals were removed very rapidly. The abundance of quartz associated with kaolinite probably meant a source of sediment at a relatively higher elevation and faster flowing streams or more rapid deposition without time enough to wash and sort clay and sand size particles.

TYPE (2)

Abnormal montmorillonite is the most predominant clay mineral constituent of the clays mentioned under Type (2). The mineral forms as much as 60 per cent total content of those clays.

Ross and Hendricks (1945) have thoroughly discussed the environment of formation of the montmorillonite group of clay minerals. In brief they are generally antithetical to those which lead to the formation of the kaolin group of minerals. The conditions of formation of montmorillonite are:

(a) Mg, Ca and Fe can be retained. No excess H+ ions.

(b) Evaporation exceeds precipitation (semi-arid environment)

(c) Stagnant water, poor leaching and arrested drainage

(d) Alkaline conditions

(e) High Si : Al ratio

Mohr and Van Baren (1954) found that the same kind of parent rock gave rise to the formation of laterite in one location and montmorillonite in another nearby location (pp. 182 - 183) under the macro climate environment. The explanation for such different mineralogical composition lies in the difference

•f chemical environment or micro-climate in them. The micro-climatic factor was responsible for the relative amount of leaching undergone by laterite and montmorillonite. Therefore it appears appropriate to consider the term climate with reference to micro-environments or micro-chemical climates which include the activity of hydrogen - ion concentration, pH, oxidation - reduction potential, Eh (Krumbein and Garrels 1952), leaching, etc. in a local restricted condition of the formation of a particular clay mineral.

From the foregoing environmental conditions it appears that a semi-arid micro-climate environment probably existed locally at particular lakes or more generally during particular epochs and that the condition favoured the formation of montmorillonite. This trend of climatic change either in time or space from heavy rainfall and less evaporation (favourable for kaolinite formation) to less precipitation and more evaporation (favourable for the formation of montmorillonite) may have given rise to the genesis of different clay minerals in the various lacustrine sediments during the Tertiary period. These physico-chemical conditions were probably present during the reactions in geological occurrences and such conditions are quite well known and understood from the laboratory experiments

of synthesis of clay minerals (Noll 1934 and 1935)

Nature of Parent Material

Another point of interest is the nature of parent material for the formation of montmorillonite. As defined by Ross and Shannon (1926) bentonite (composed dominantly of montmorillonite) is formed by the chemical alteration of glassy igneous material, usually tuff of volcanic ash. However the author found no evidence for the origin from volcanic ash in any of the clay samples; there is no associated suite of non-clay minerals (biotite, hornblende, etc.) characteristic of igneous materials nor of shards and glassy material. Therefore a volcanic origin cannot be ascribed to the genesis of montmorillonite in the sediments. The formula and composition (more silica and less alumina than kaolinite) of montmorillonite suggests that the parent rock was probably dolerite - rich in Ca, Mg and Fe. Magnesium is essential in the composition of montmorillonite, since it substitutes aluminium in the octahedral layer, and the compensation for the deficit of electric charge is made up by calcium and other alkali metals. Montmorillonite contains 2 - 3 times as much silica as alumina. H^+ ion is relatively less abundant to cause hydrolysis in dolerites, but most of the metal cations

and silica remained active in the system and the water was too scanty to leach them away (under semi-arid conditions of less rainfall and more evaporation). The divalent cations calcium and magnesium flocculated silica and held it to form a silica-rich clay mineral - montmorillonite. The reaction solution was alkaline. Probably these conditions of arrested drainage and restricted oxidation existed and favoured the formation and preservation of montmorillonite in certain lakes or at certain times during the Tertiary Period.

The clays mentioned under type (2) were characterised by an abnormal montmorillonite and a probable cause of its formation has already been discussed in the last chapter.

As described in a previous chapter, in the laboratory a normal type of montmorillonite can be converted to an abnormal montmorillonite by a process of dehydration (at high temperature) and rehydration (at atmospheric temperature and pressure), a similar probable mechanism in nature can be attributed to the formation of abnormal montmorillonite. Clays from Glenora (1 and 1A), Plenty (3), Cornelian Bay (5), Macquarie Plains (16) and One Tree Point, Sandy Bay (19) are associated with extensive basalt flows. These clays might have been dehydrated by the outpouring of the

basalts to favour the formation of abnormal montmorillonite, but these are exceptions in clays from Sandy Bay (10 and 11) which contain abnormal montmorillonite but not associated with basalts now. Similarly there is another exception of clay from Mangalore (15) which is post-basaltic in age and is still characterised by abnormal montmorillonite.

The nature of clay sample (2) was described as fluviatile by Wooley (1956), but his interpretation is not favoured, because the predominant mineral is montmorillonite. In the fluviatile types of sediment one would expect a certain amount of leaching action which would help kaolinite to grow. In the writer's opinion the clay is probably of lacustrine origin and was deposited under the same environmental conditions as those discussed under type (2).

Diagenetic Change

It appears that there was no diagenetic change with the accumulation of the clays as revealed by the clays (8, 10 and 11). It is not surprising, therefore, that no clay mineral variations were found with 36' depth in the latter.

TYPE (3)

Mixed layer minerals having random interstratification

of illite and montmorillonite (in the ratio of 3:2) may have formed as an intermediate stage in the alteration of micas and other silicates and little can be said about their actual mode of formation.

It seems from the clay mineral compositions of type (3) that some forms (3:2) of interstratification of illite in montmorillonite are probably more stable than the others, although one might have expected all transition stages of weathering from illite to montmorillonite.

TYPE (4)

The joint presence of kaolinite and montmorillonite in these clays suggests that the source areas had a warm climate at some places and a cool cimate at others and that one micro-climate followed a different one with/out equilibrium being attained.

Clay sample (8) which is residual in origin and of the type (4) suggests that alternated conditions of abundant rainfall and less evaporation and semi-arid environmental micro-climate probably existed.

TYPE (5)

The clays (9 and 12) overlying the bauxite are not lake deposits but are of Tertiary age. They are primary in origin and kaolinite formed due to the resilication of the bauxitic material.

In the initial stages alkalie amd alkaline earth metals were removed with silica by the process of strong leaching - at the surface where oxygen was in excess. Strong oxidizing conditions apparently favoured the formation of gibbsite.

CONCLUSIONS

The foregoing tentative environmental interpretations were based on an allogenic nature of the clay minerals and the writer feels that is is too early to assess the importance of clay minerals as indicators of environment of deposition. More work remains to be done in thisfield.

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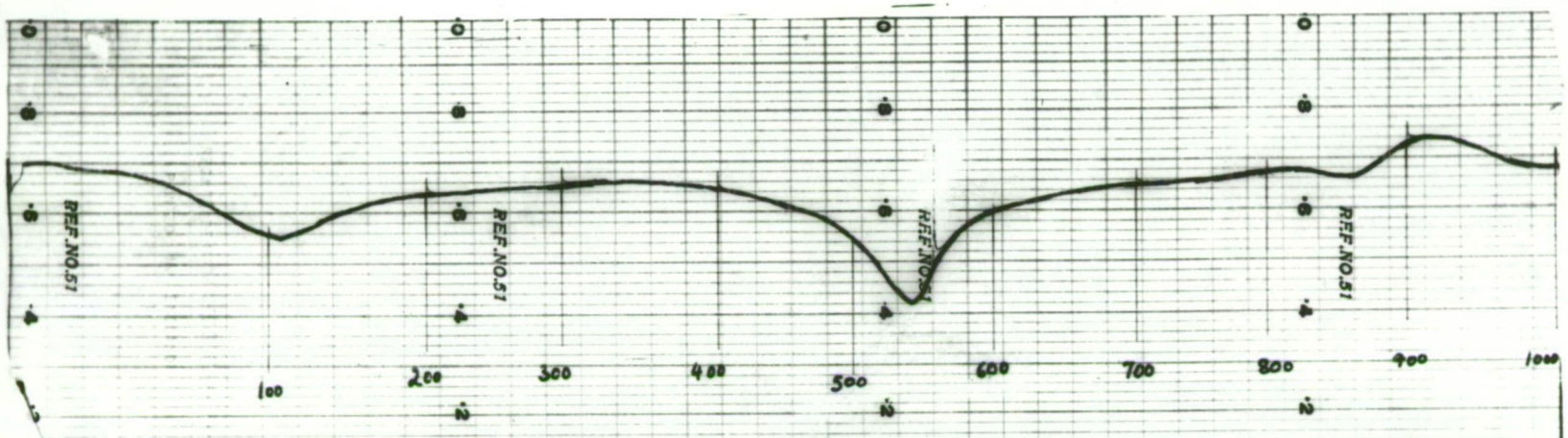

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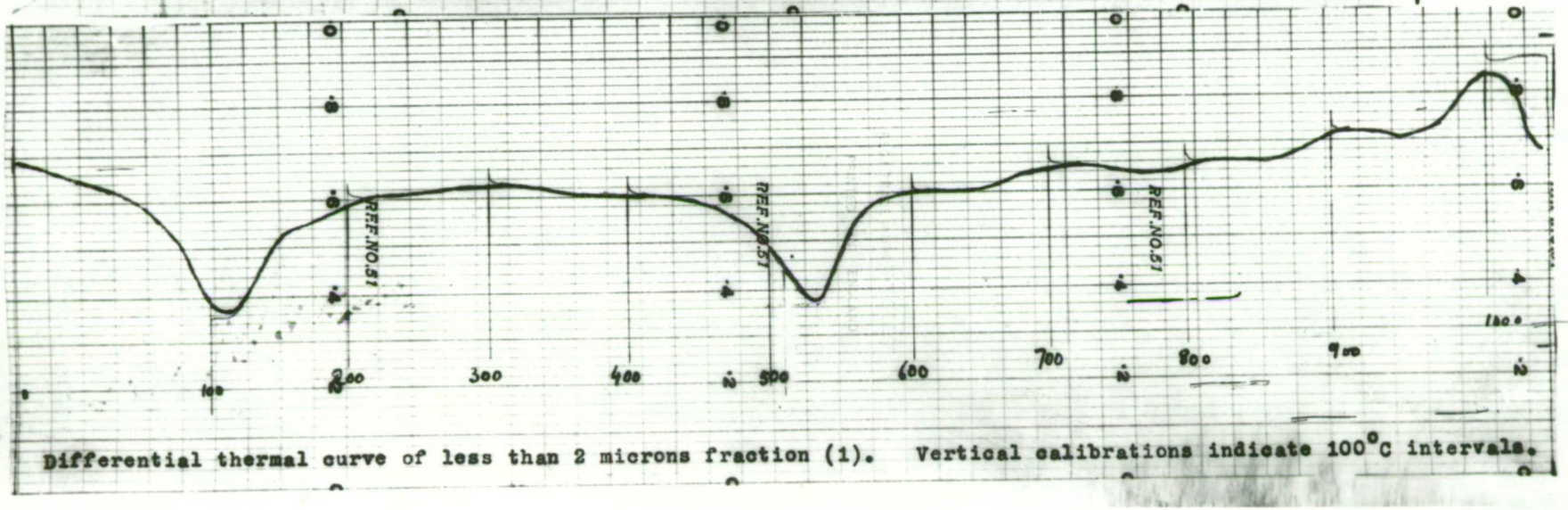

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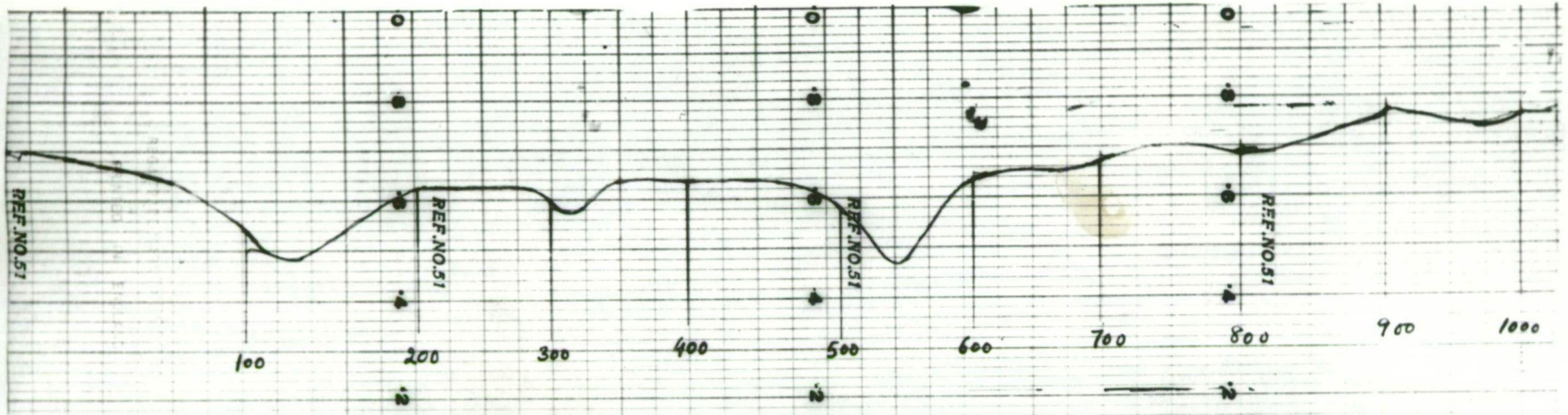

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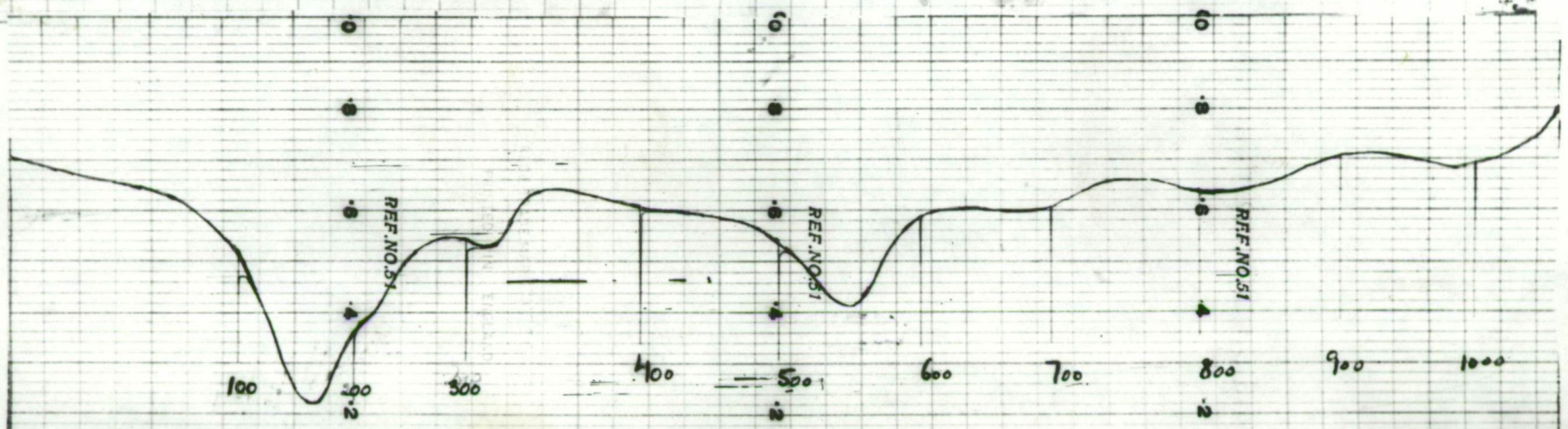

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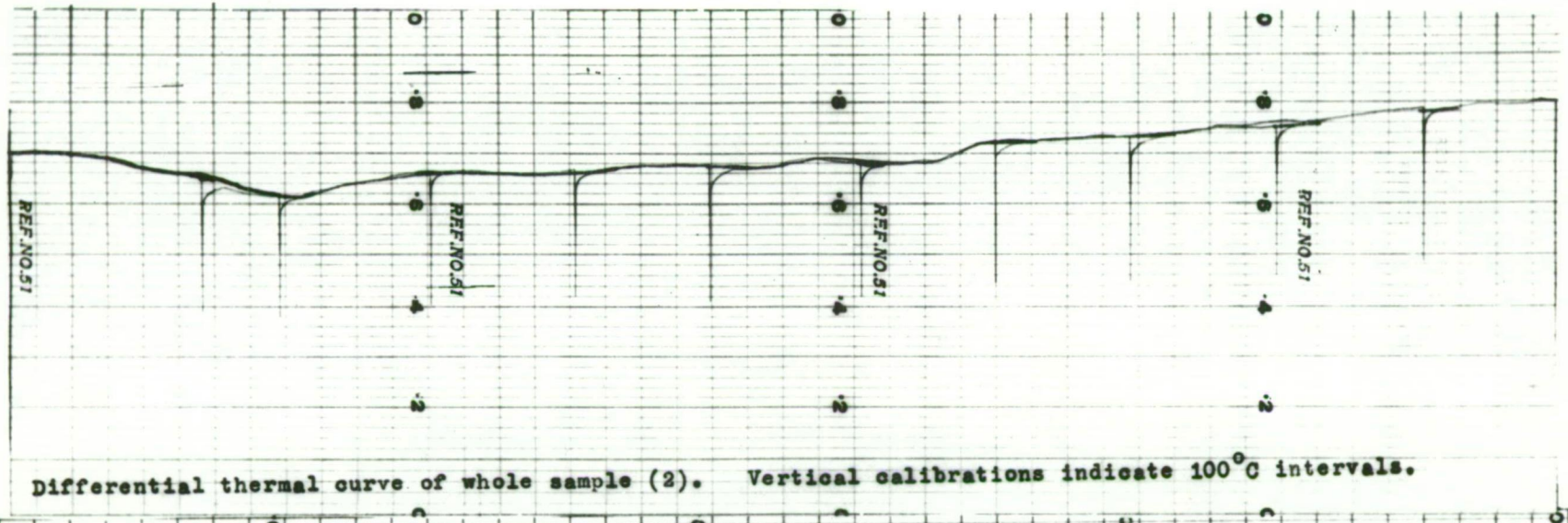

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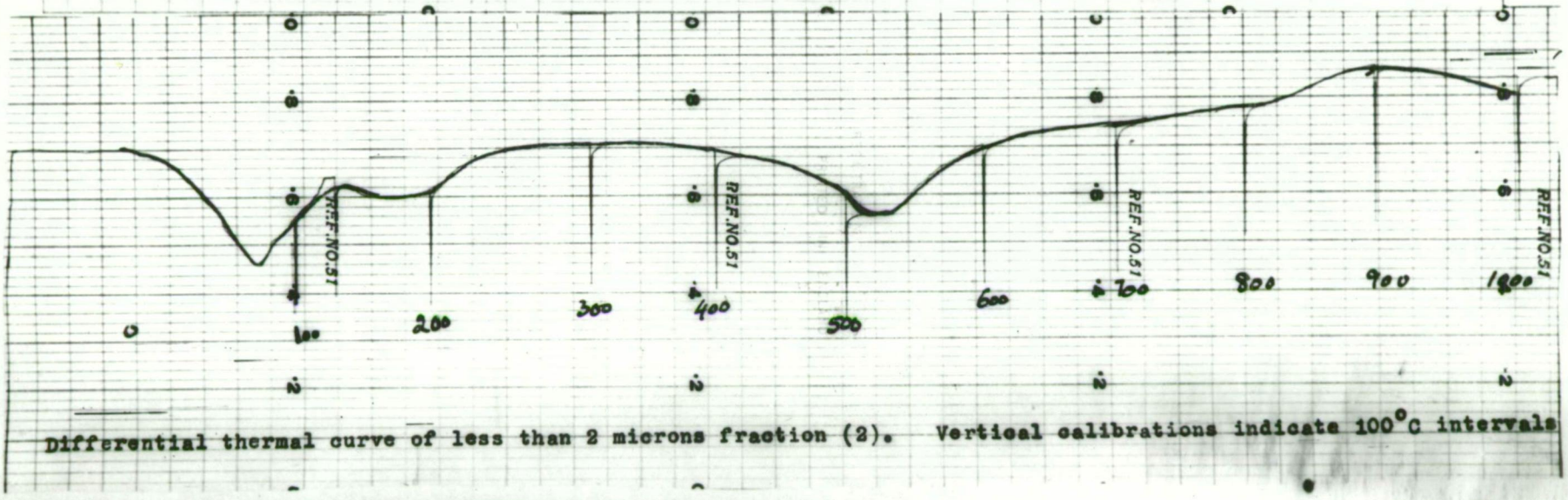

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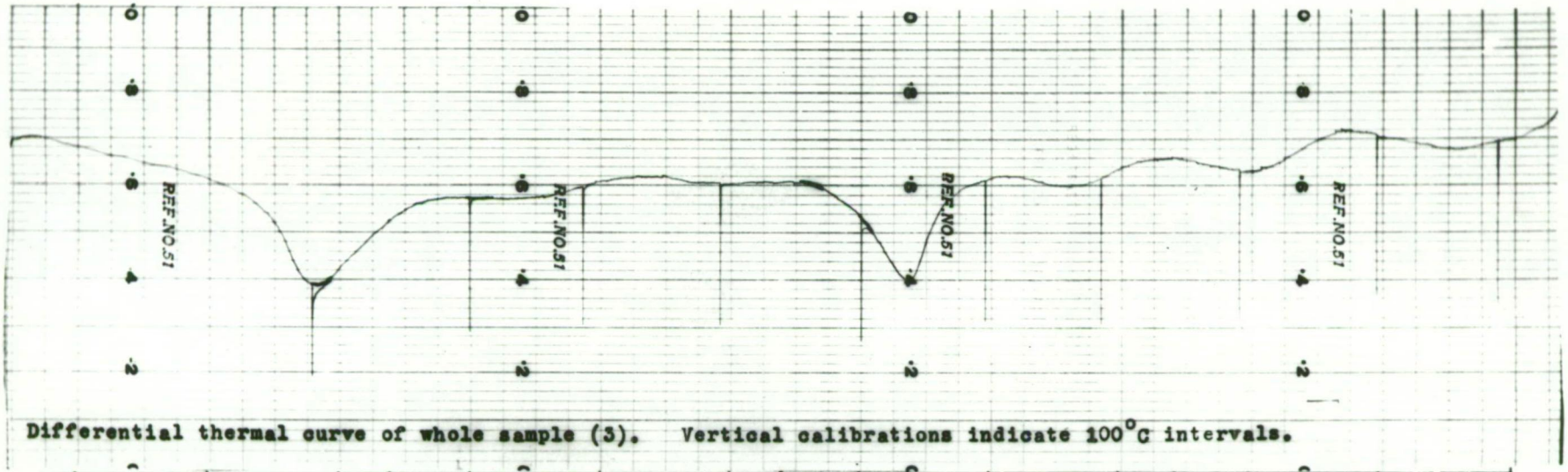

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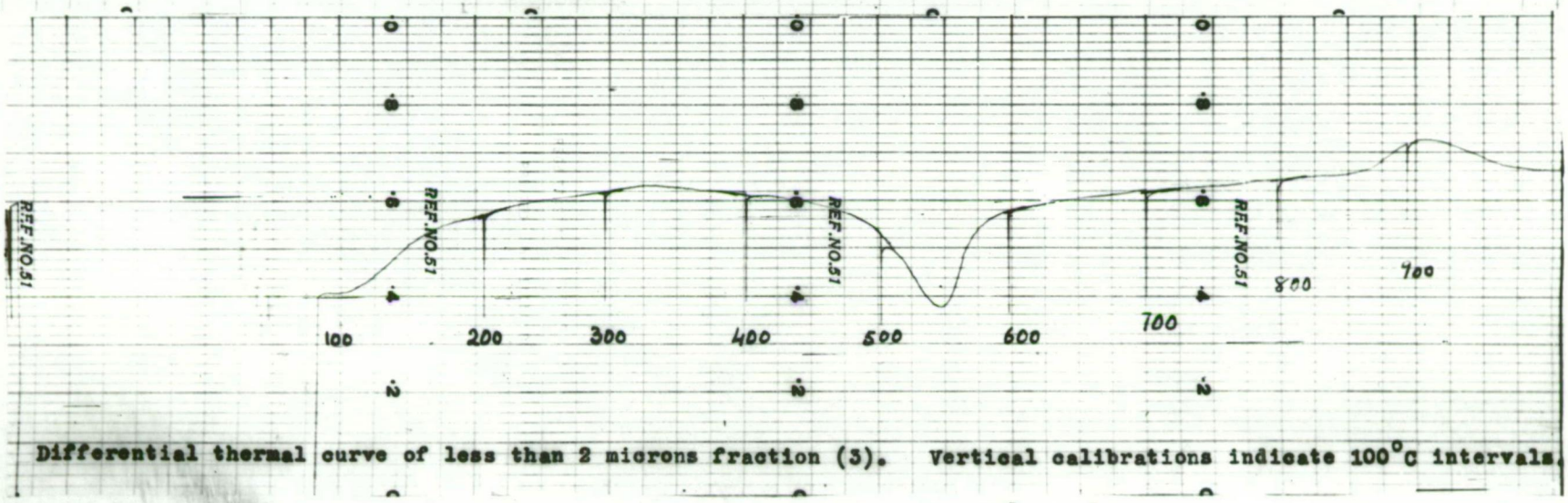

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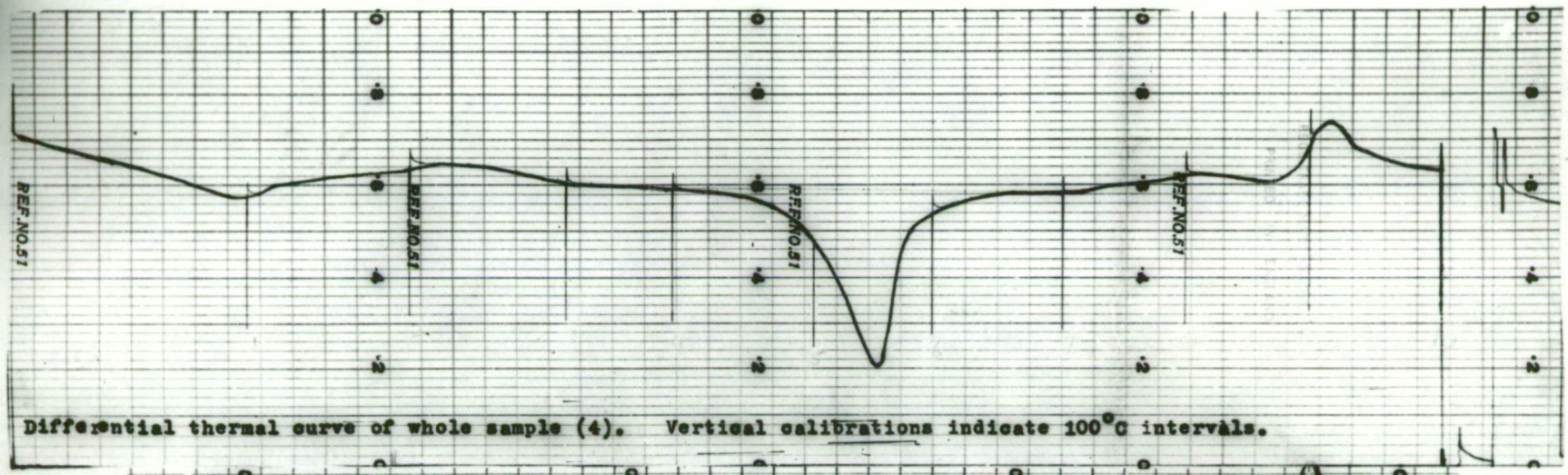

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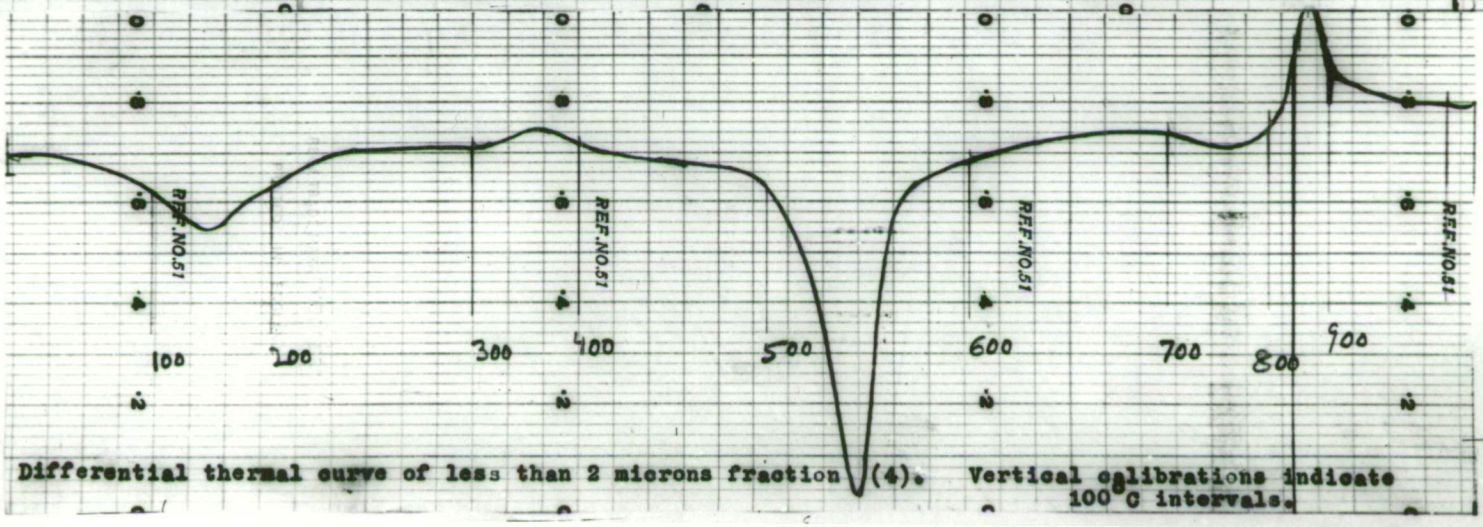

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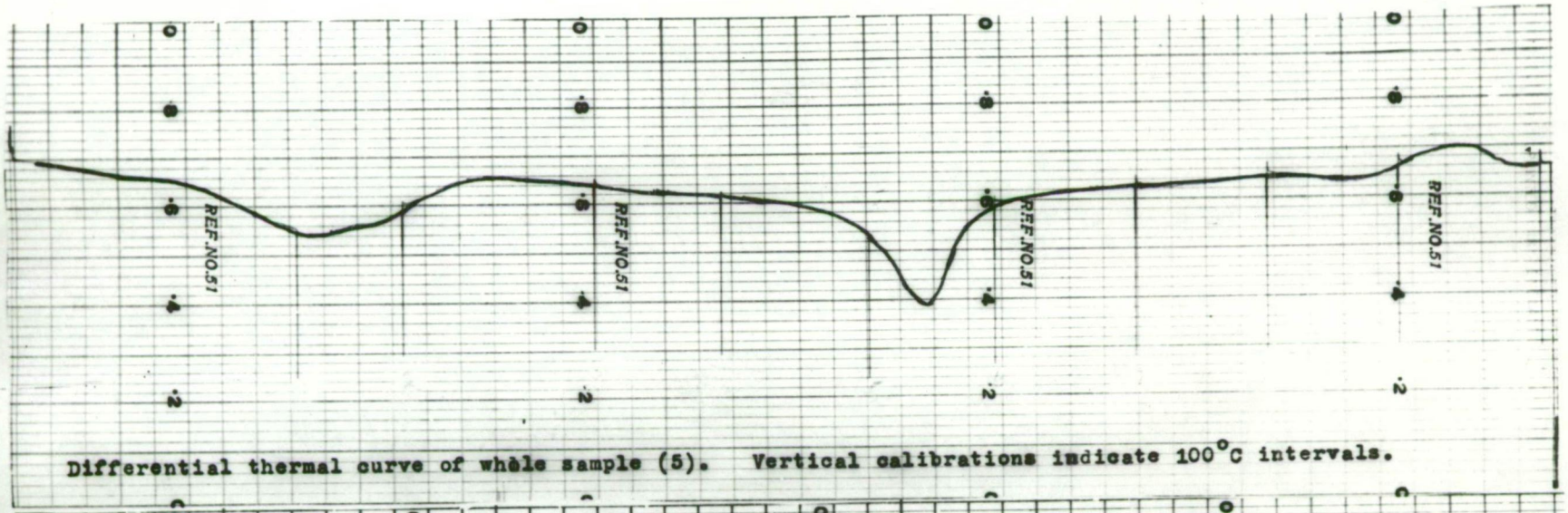

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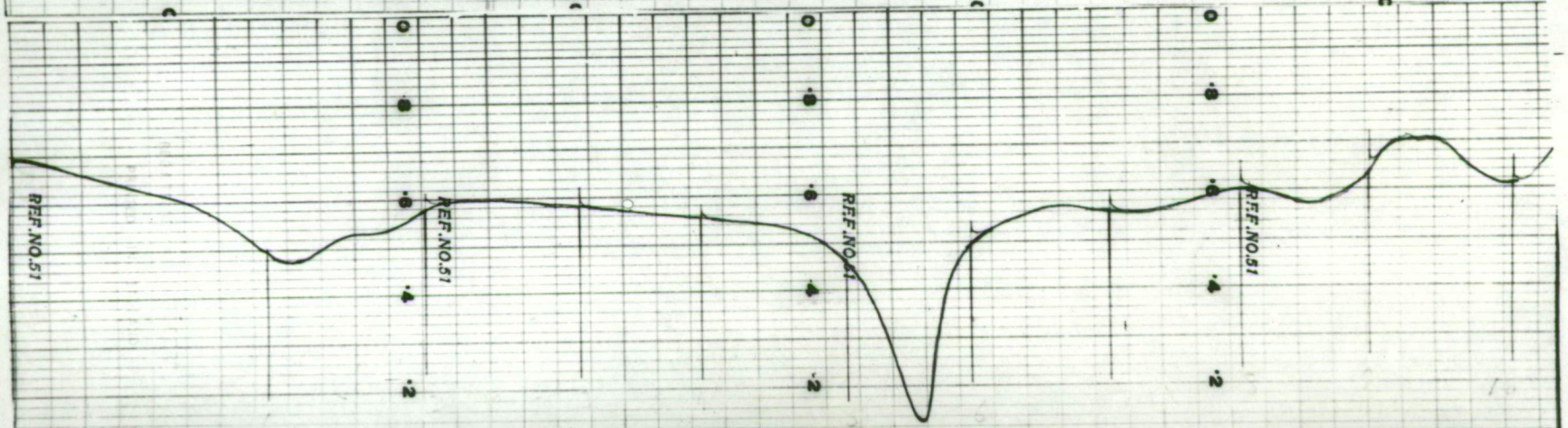

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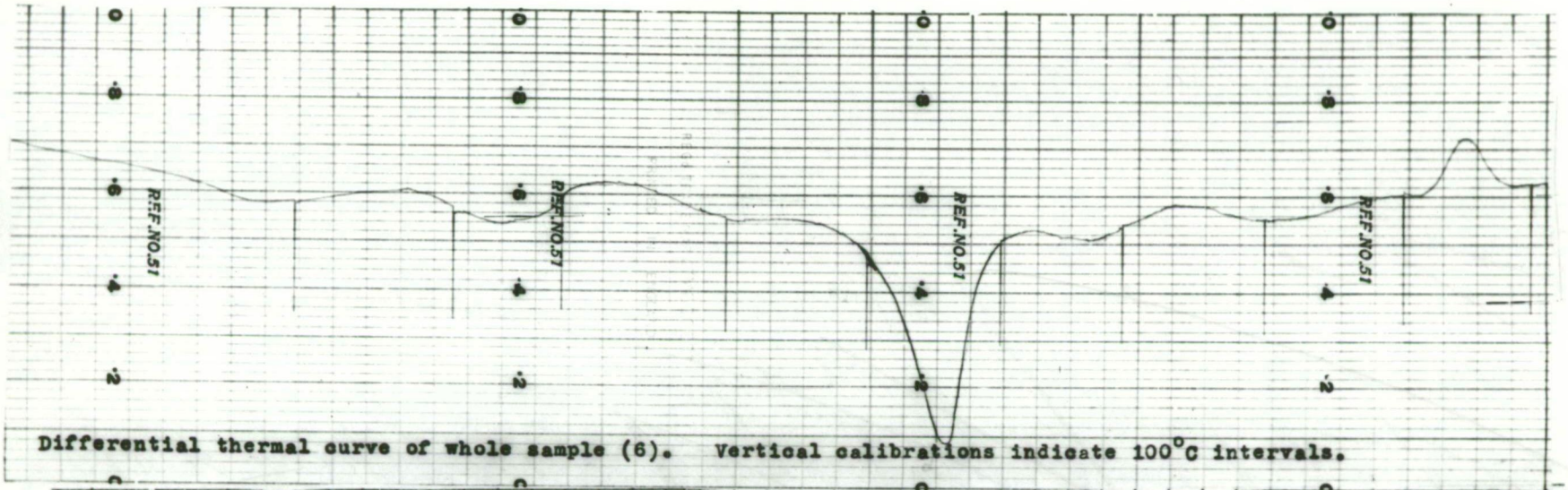

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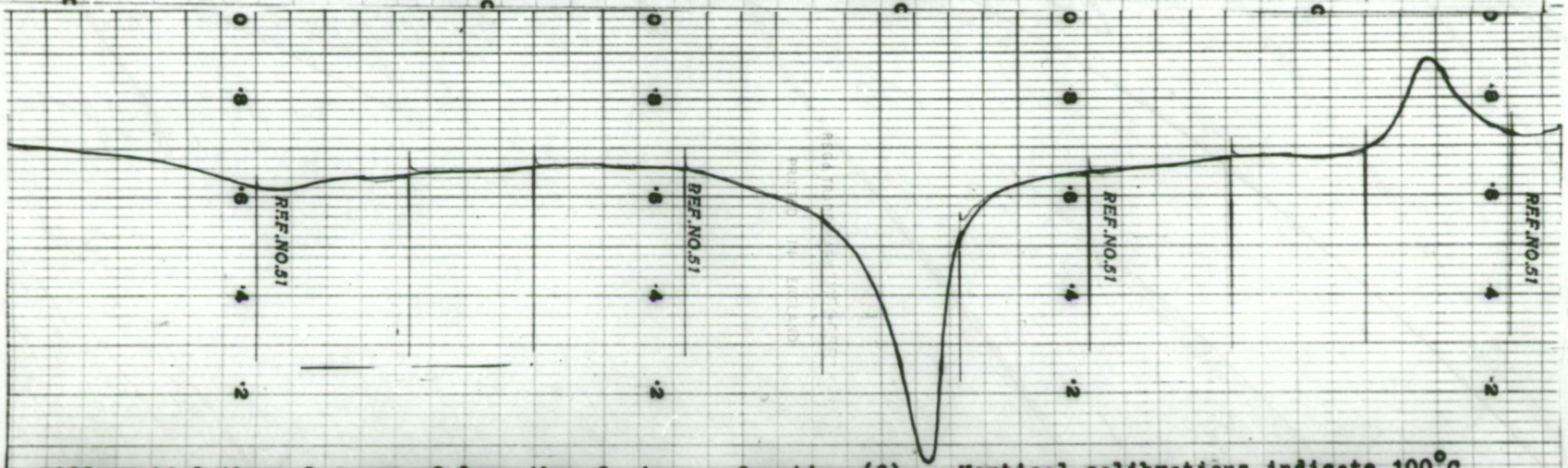

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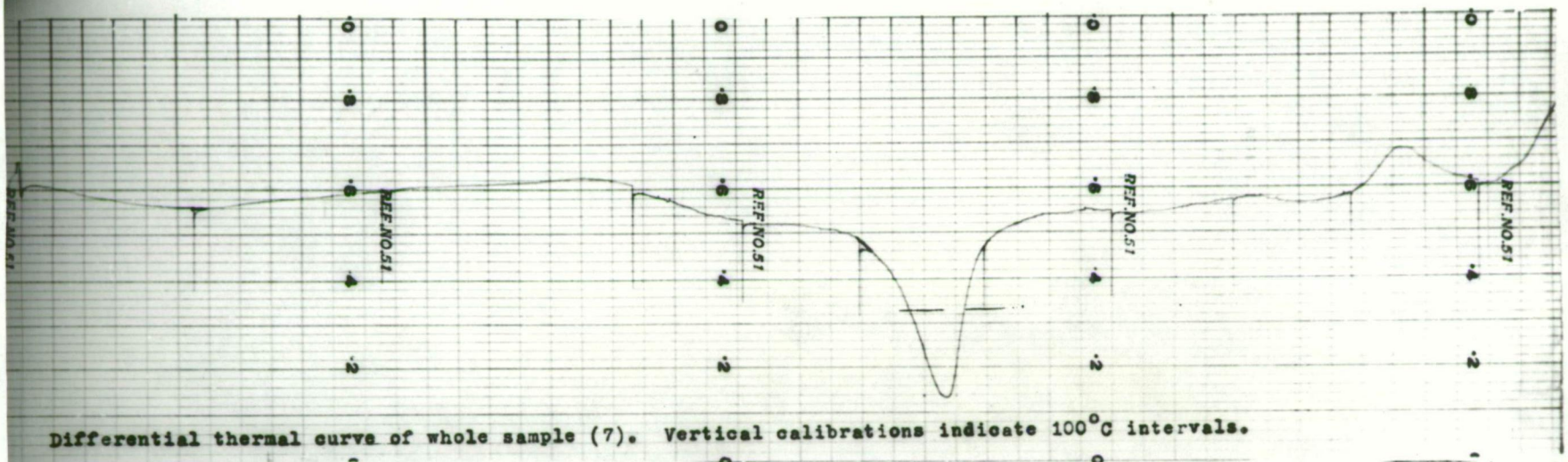

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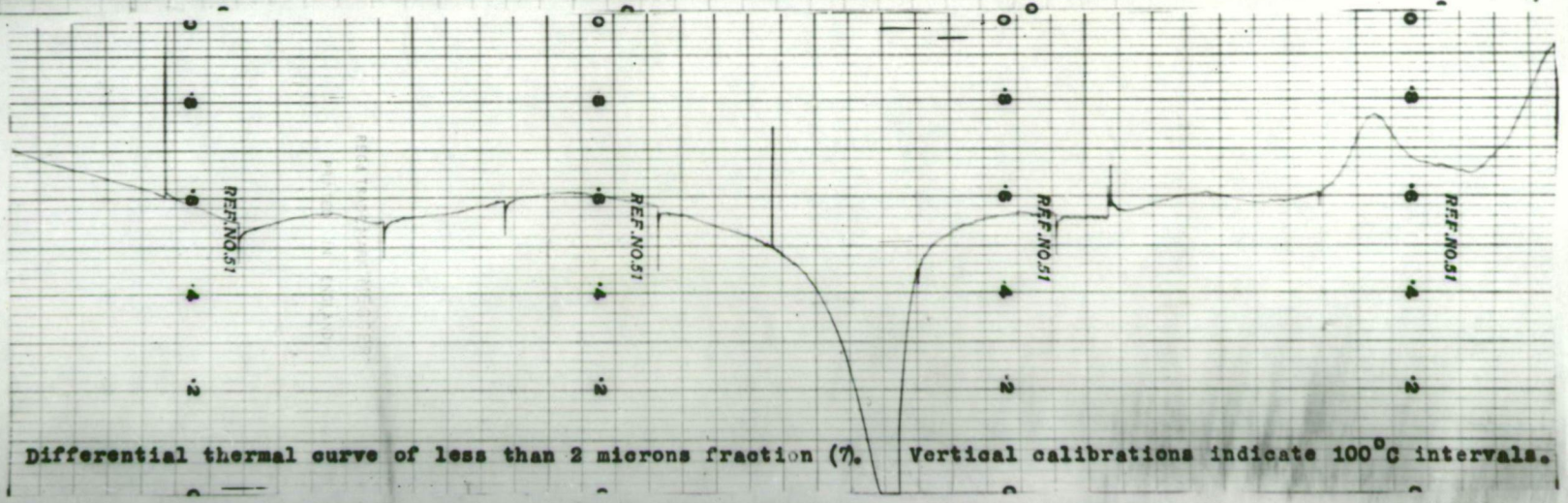

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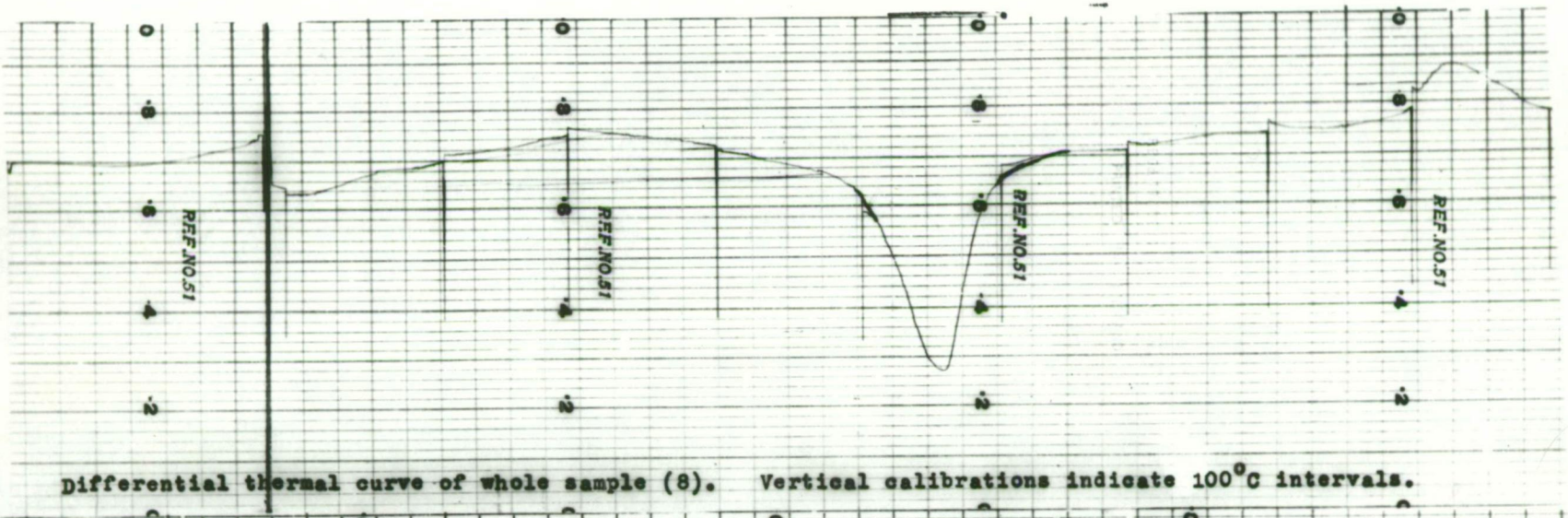

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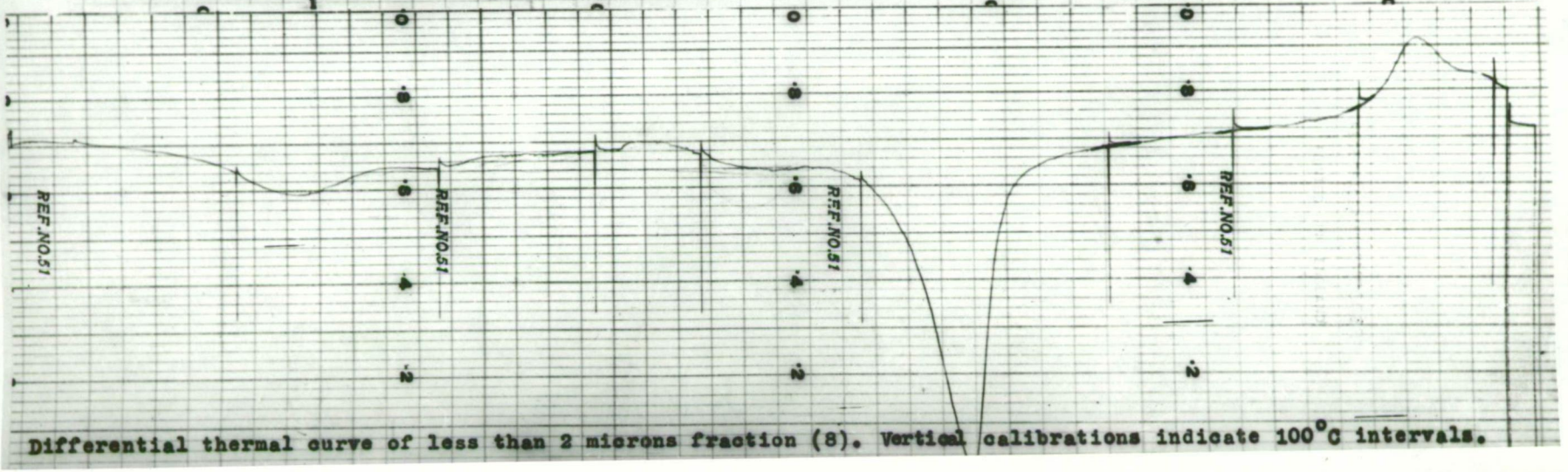

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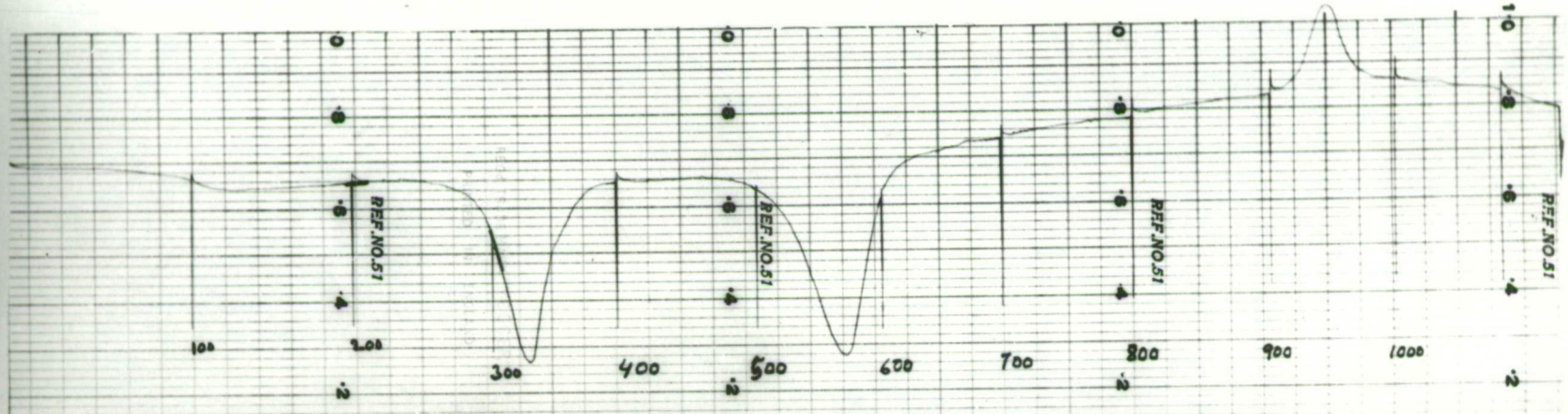
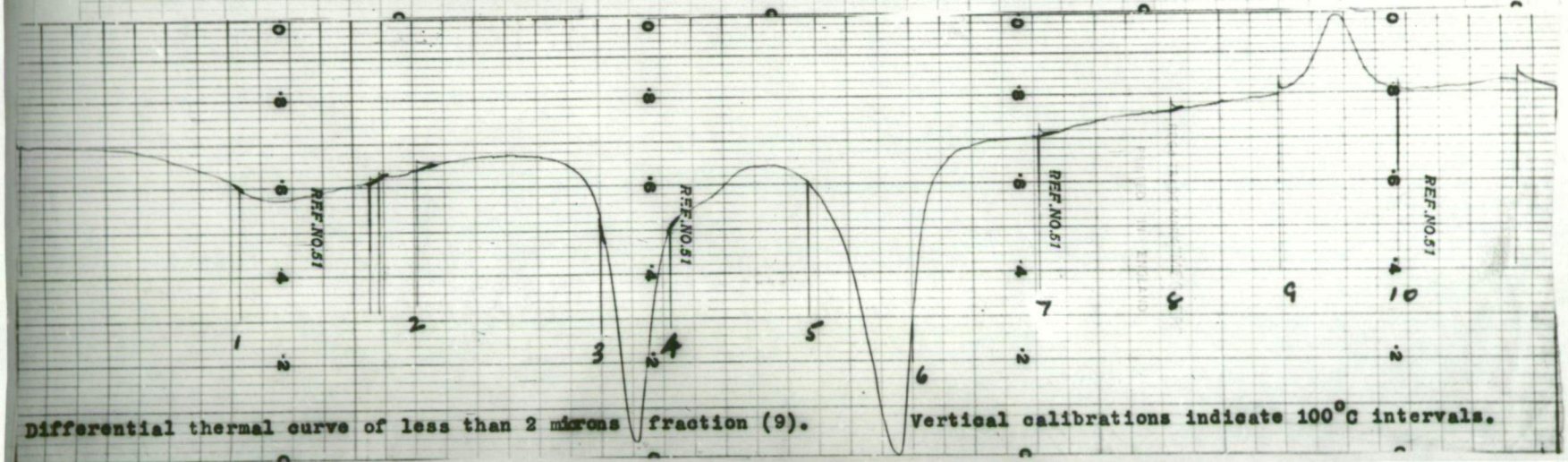
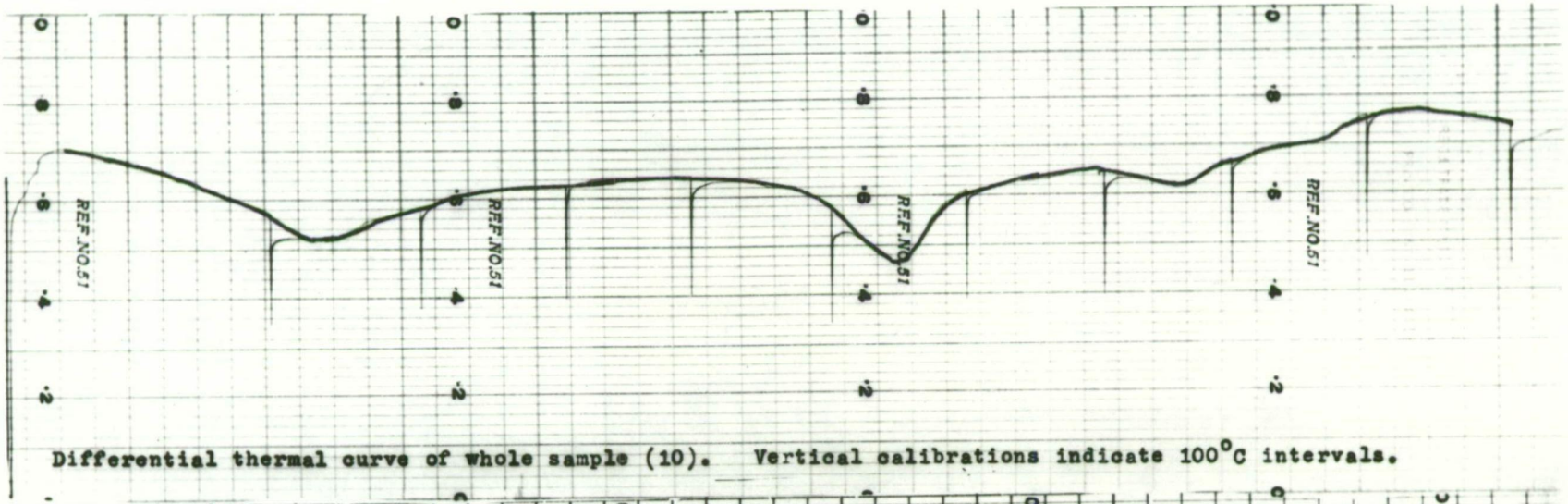


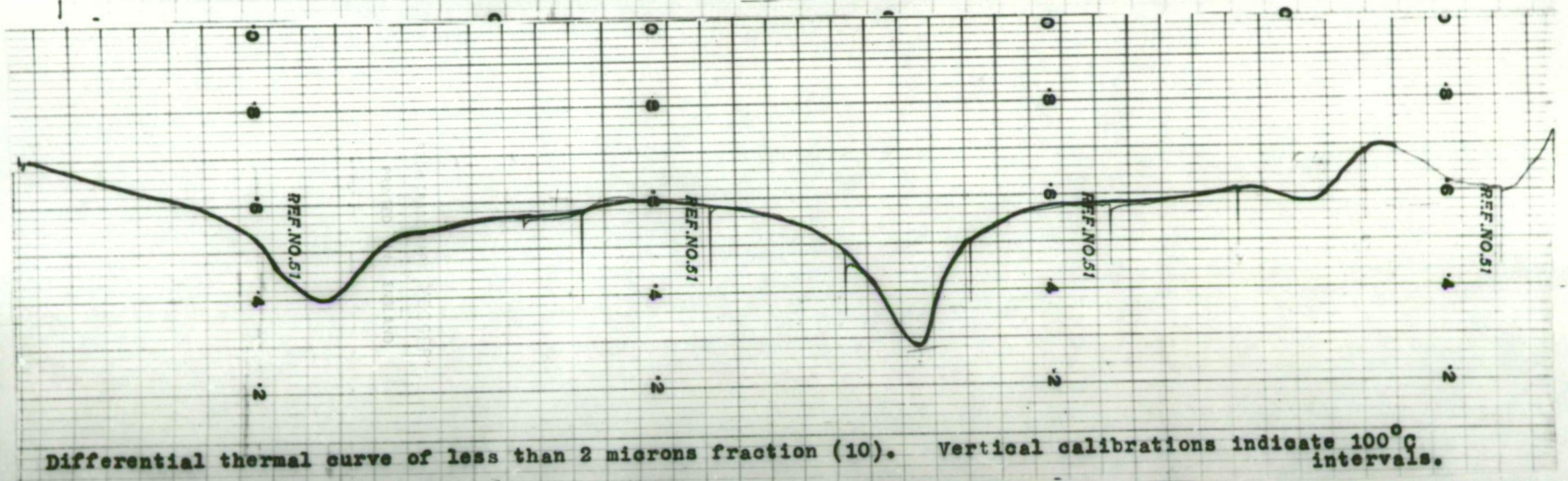
Differential thermal curve of whole sample (9). Vertical calibrations indicate 100°C intervals.



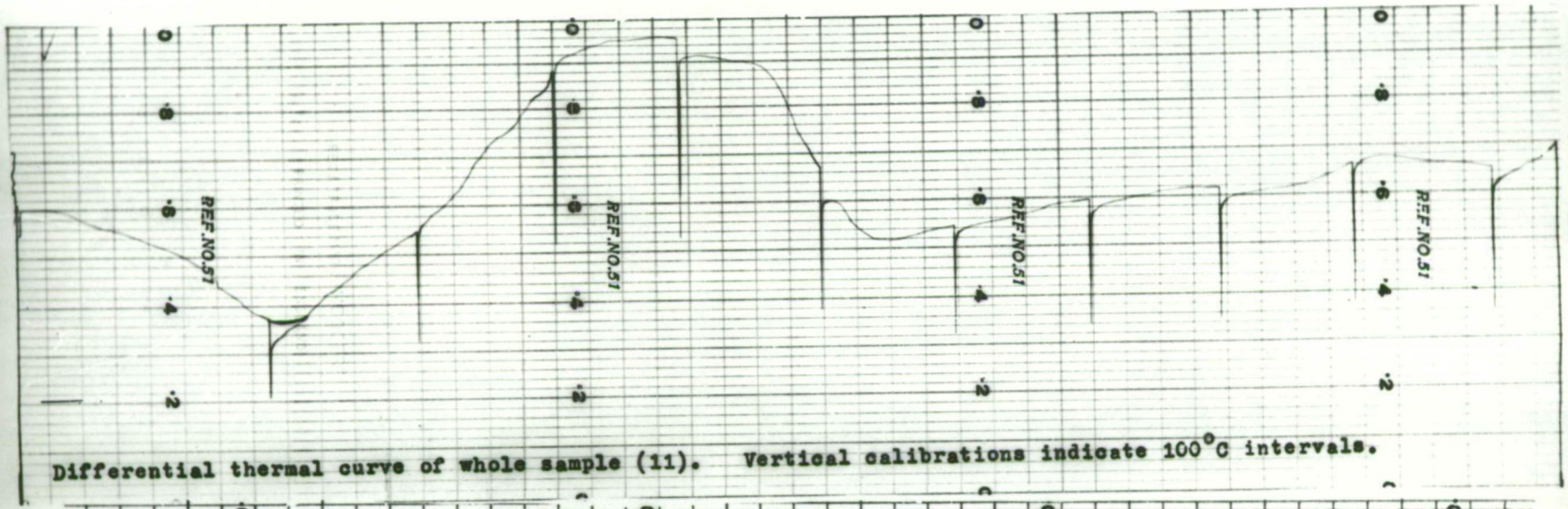
Differential thermal curve of less than 2 microns fraction (9). Vertical calibrations indicate 100°C intervals.



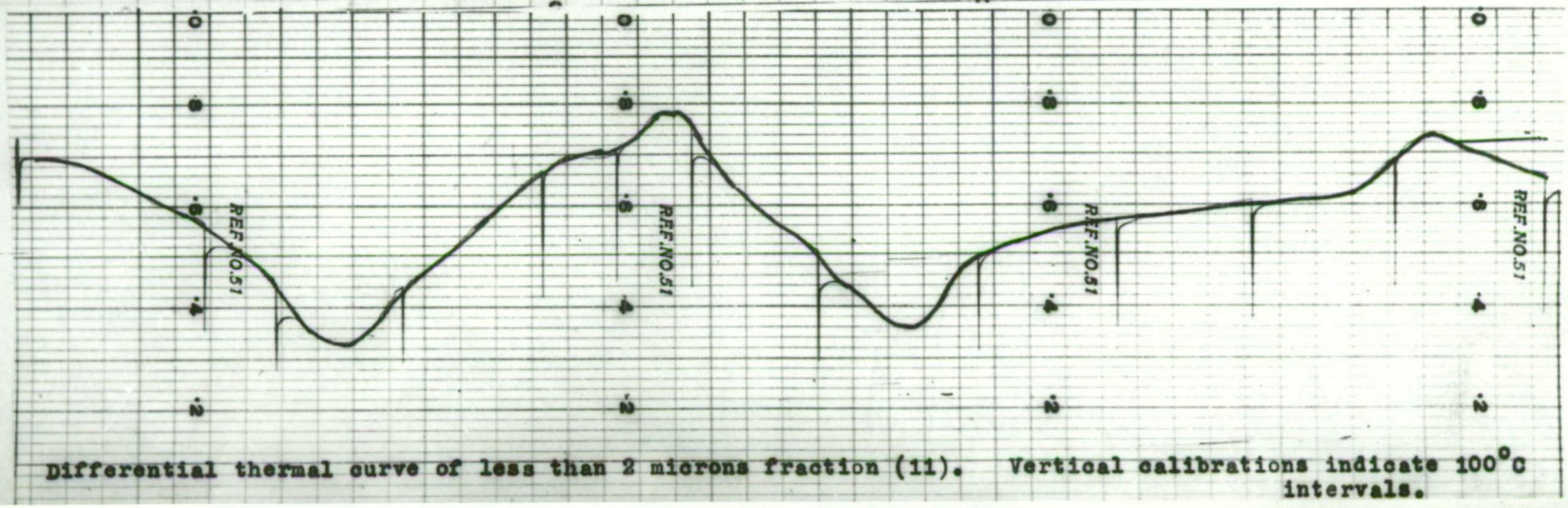
Differential thermal curve of whole sample (10). Vertical calibrations indicate 100°C intervals.



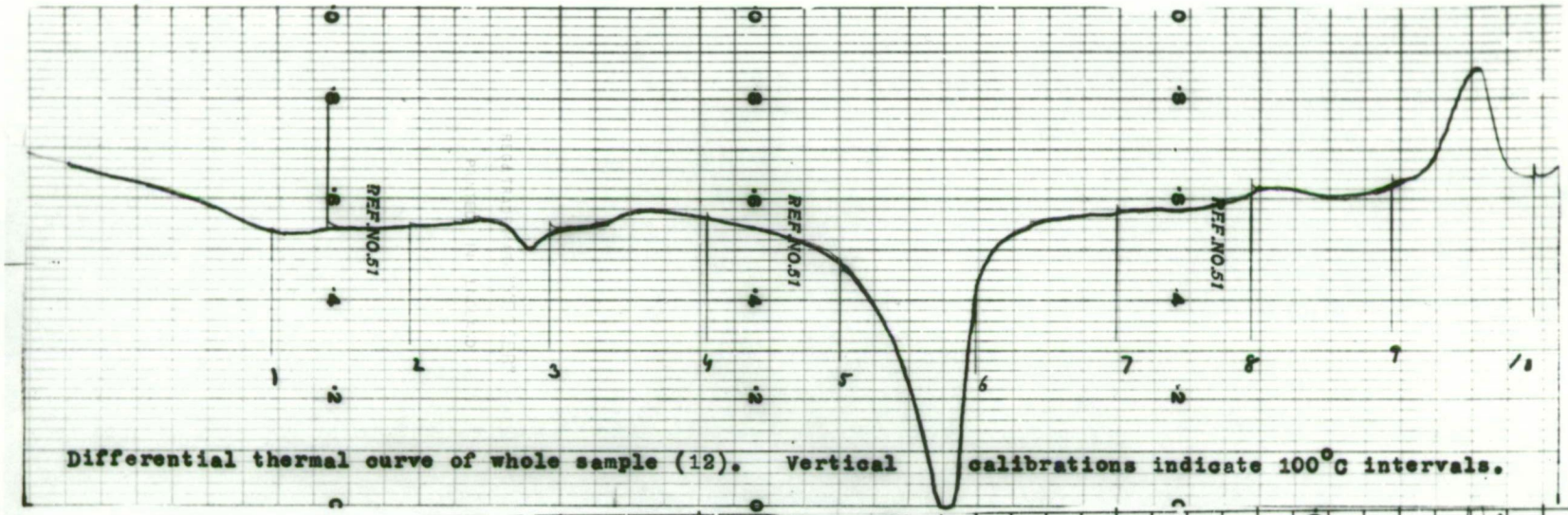
Differential thermal curve of less than 2 microns fraction (10). Vertical calibrations indicate 100°C intervals.



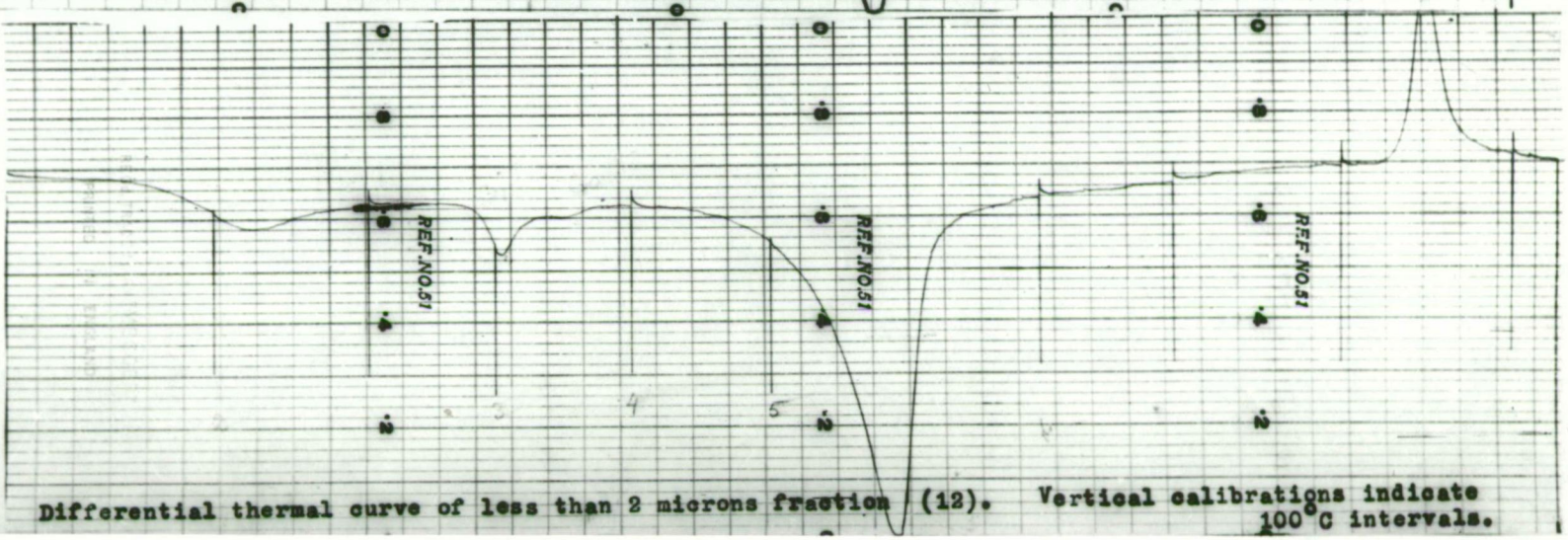
Differential thermal curve of whole sample (11). Vertical calibrations indicate 100°C intervals.



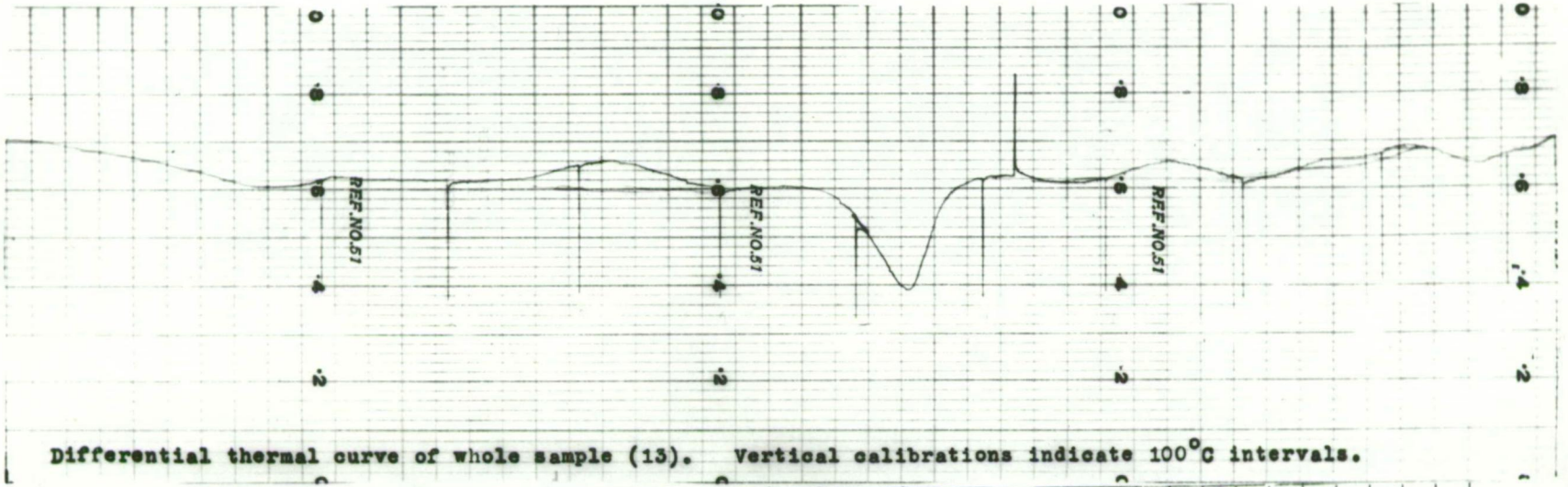
Differential thermal curve of less than 2 microns fraction (11). Vertical calibrations indicate 100°C intervals.



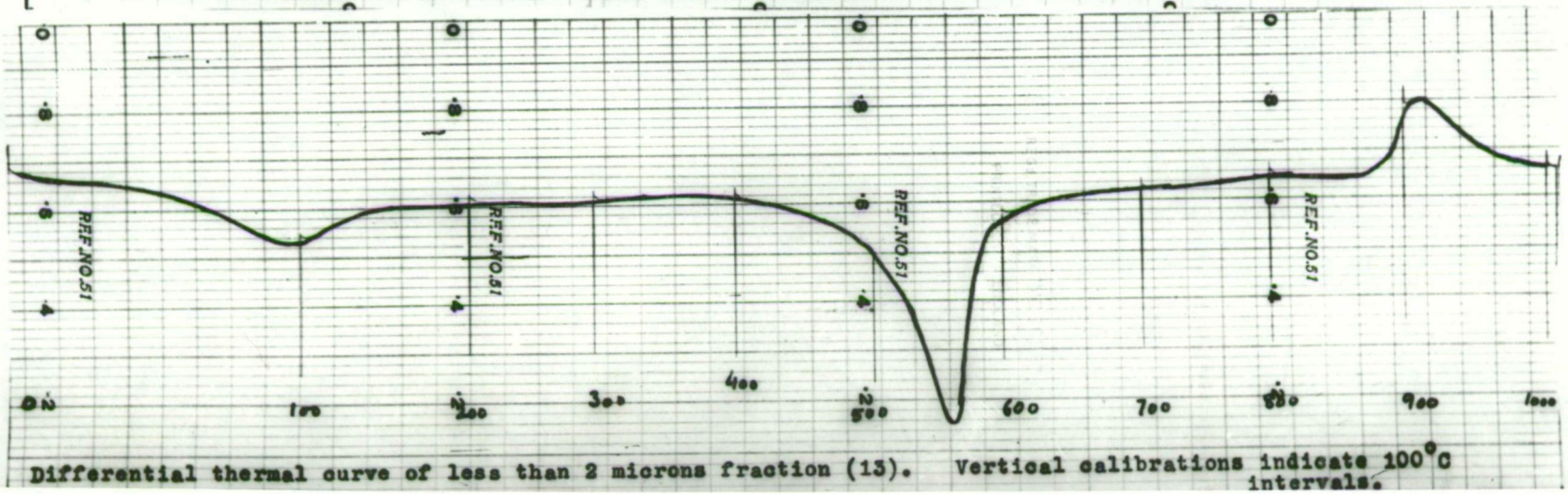
Differential thermal curve of whole sample (12). Vertical calibrations indicate 100°C intervals.



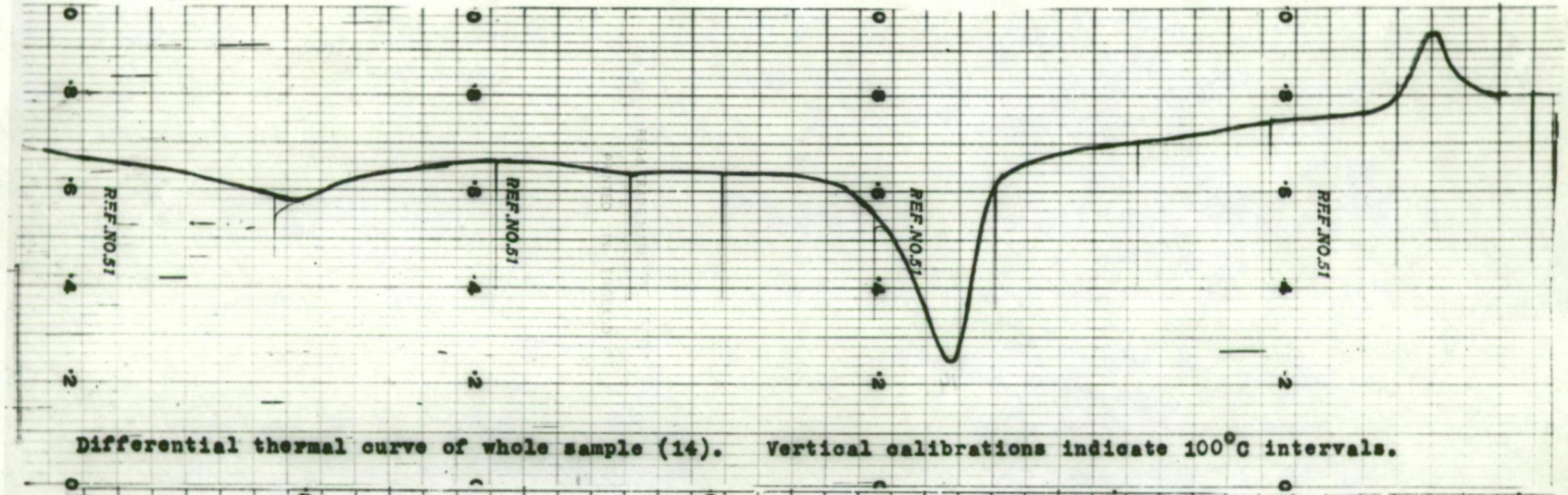
Differential thermal curve of less than 2 microns fraction (12). Vertical calibrations indicate 100°C intervals.



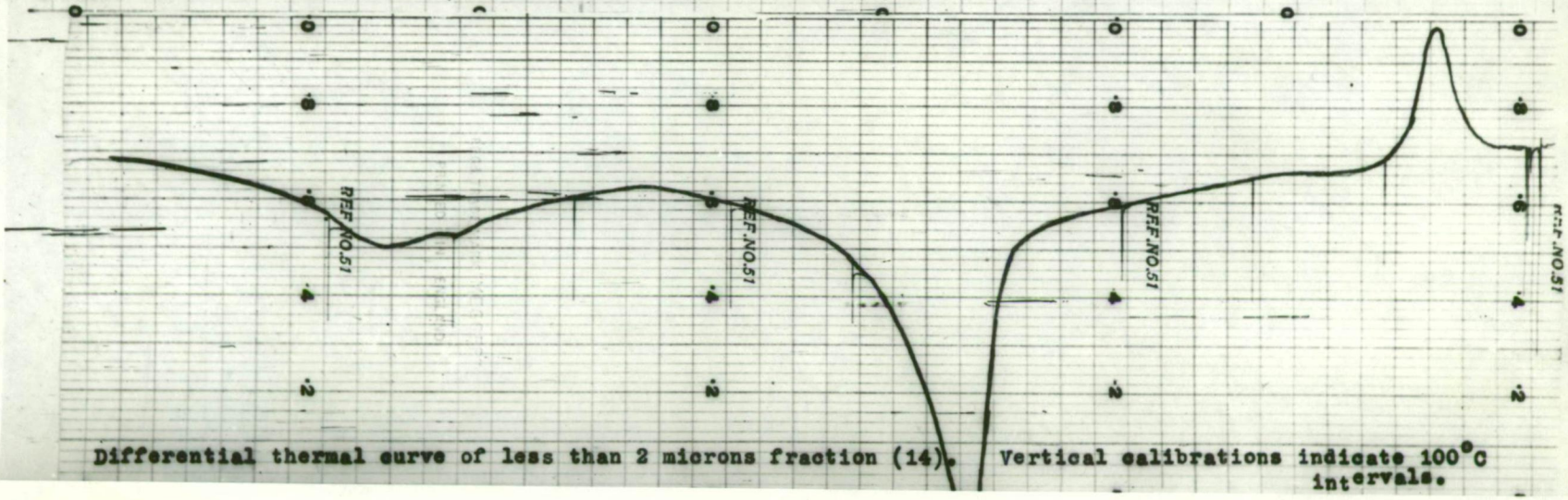
Differential thermal curve of whole sample (13). Vertical calibrations indicate 100°C intervals.



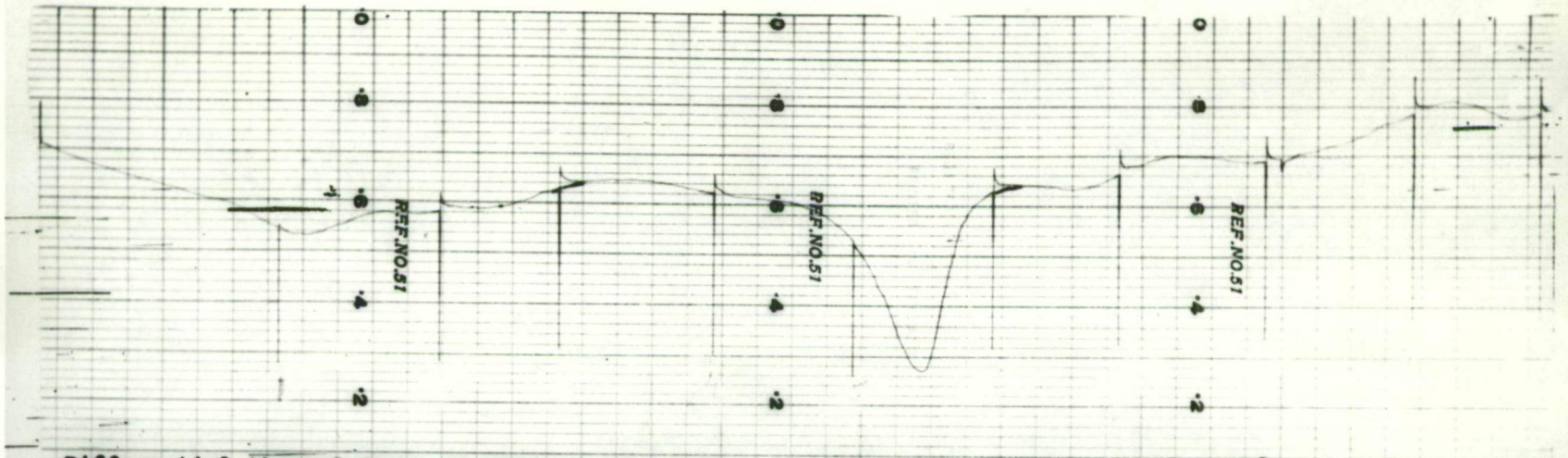
Differential thermal curve of less than 2 microns fraction (13). Vertical calibrations indicate 100°C intervals.



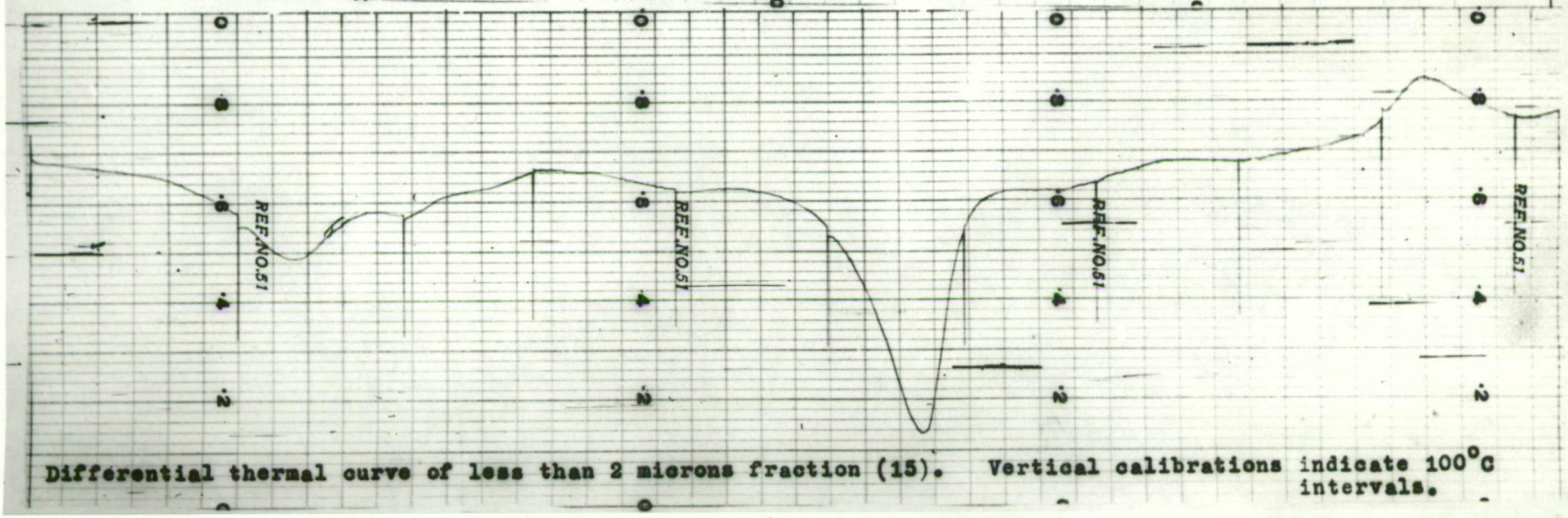
Differential thermal curve of whole sample (14). Vertical calibrations indicate 100°C intervals.



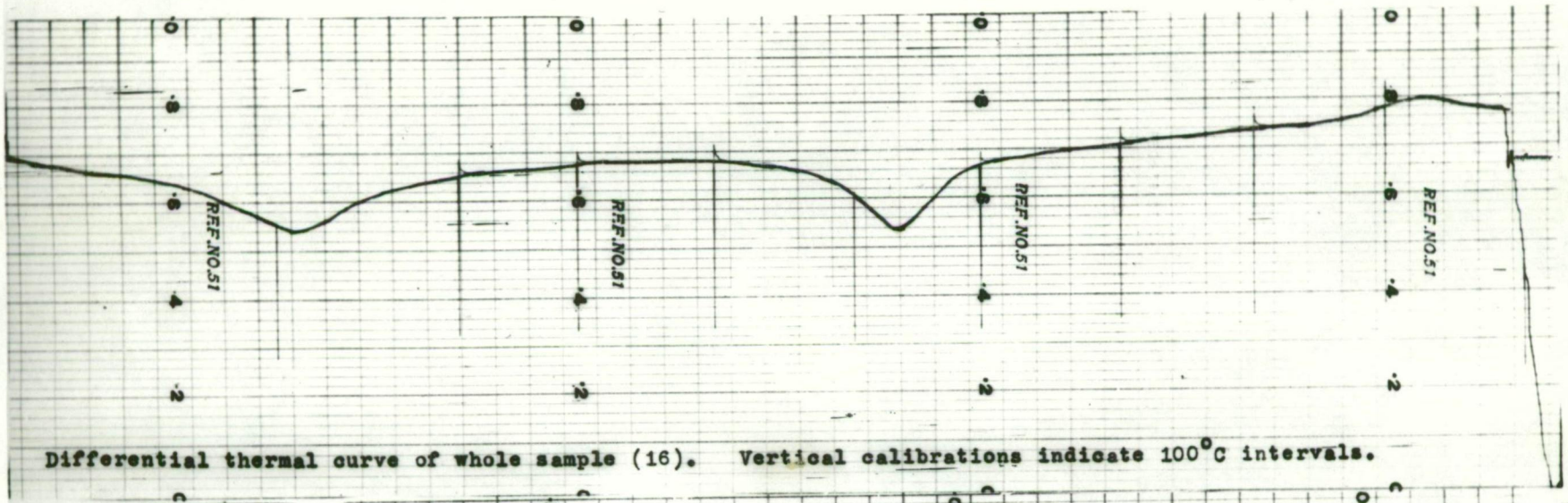
Differential thermal curve of less than 2 microns fraction (14). Vertical calibrations indicate 100°C intervals.



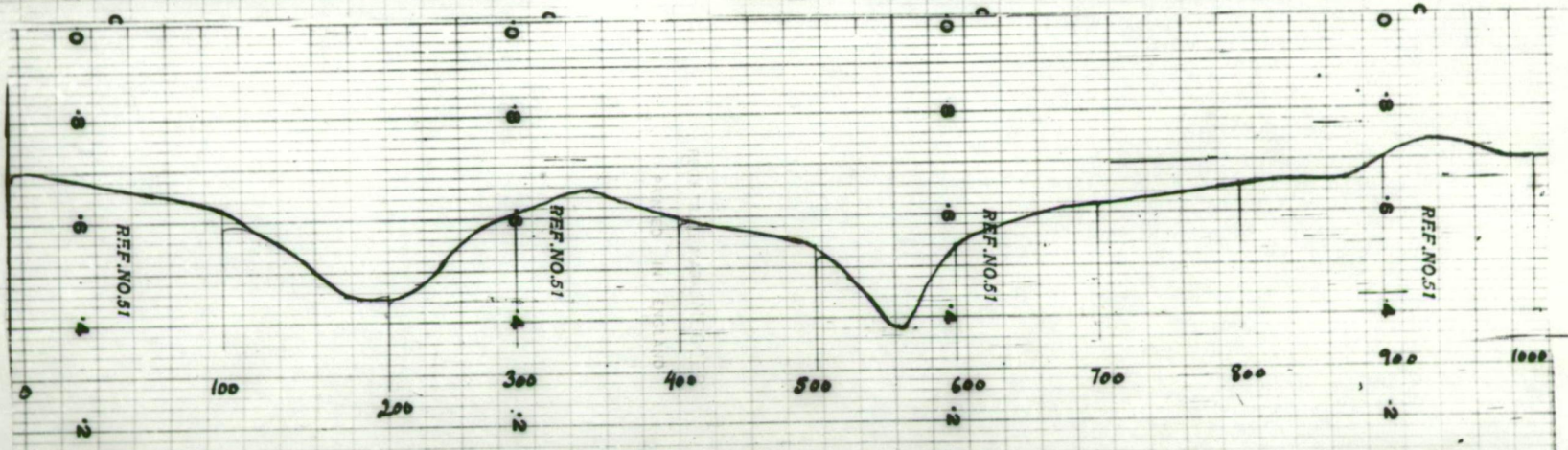
Differential thermal curve of whole sample (15). Vertical calibrations indicate 100°C intervals.



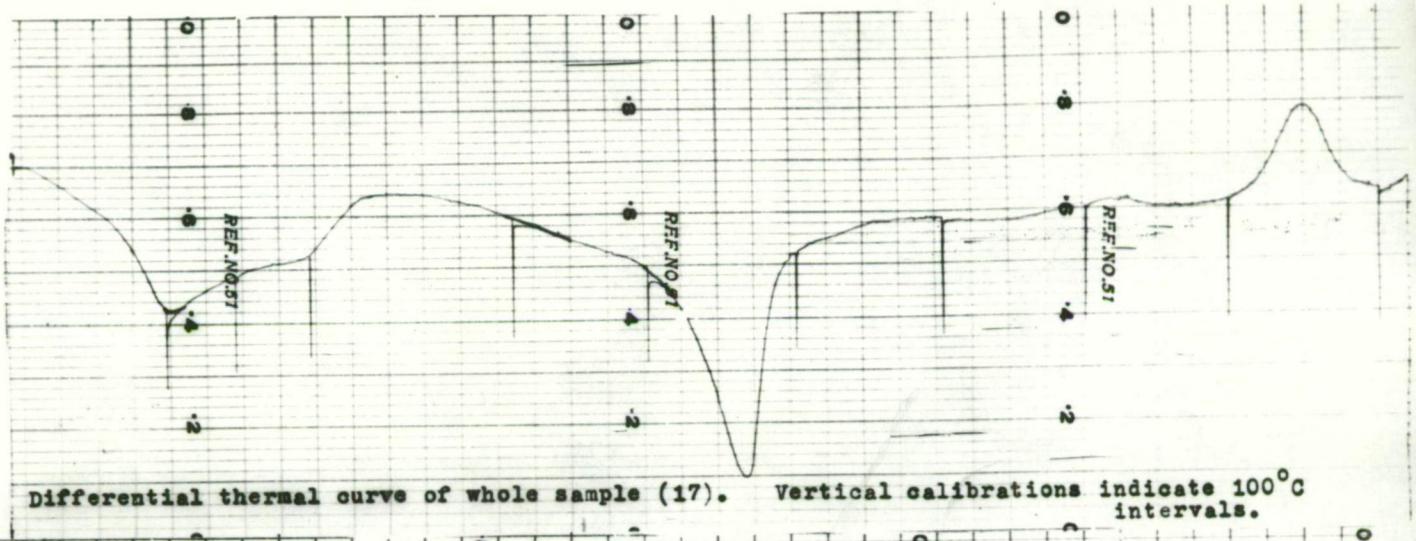
Differential thermal curve of less than 2 microns fraction (15). Vertical calibrations indicate 100°C intervals.



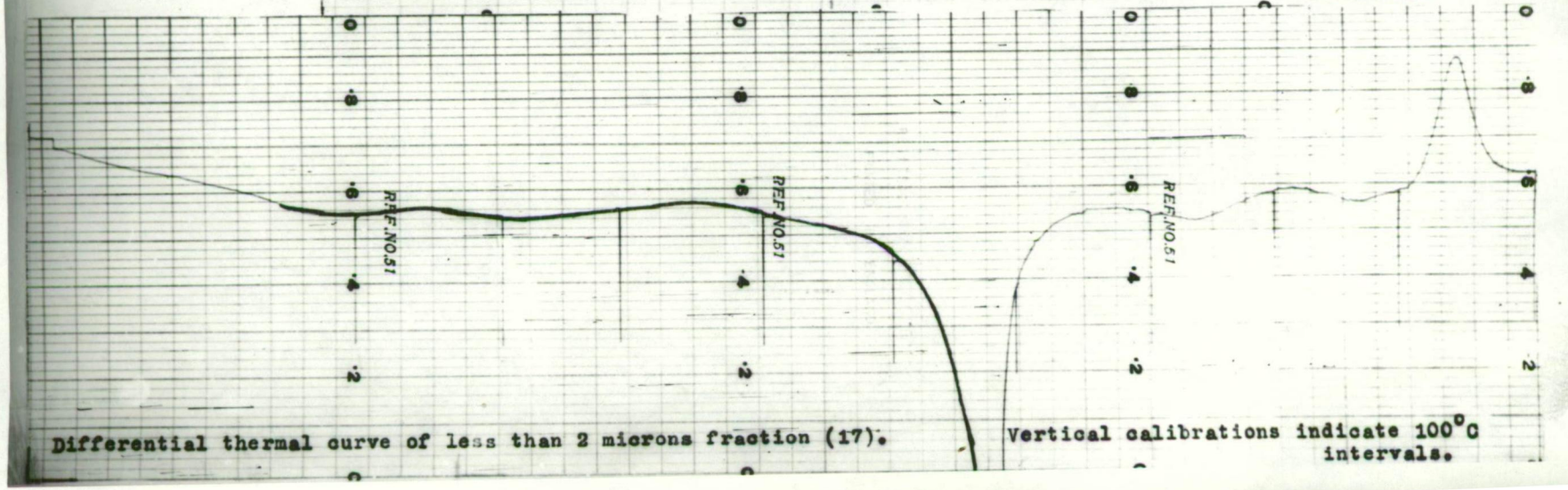
Differential thermal curve of whole sample (16). Vertical calibrations indicate 100°C intervals.



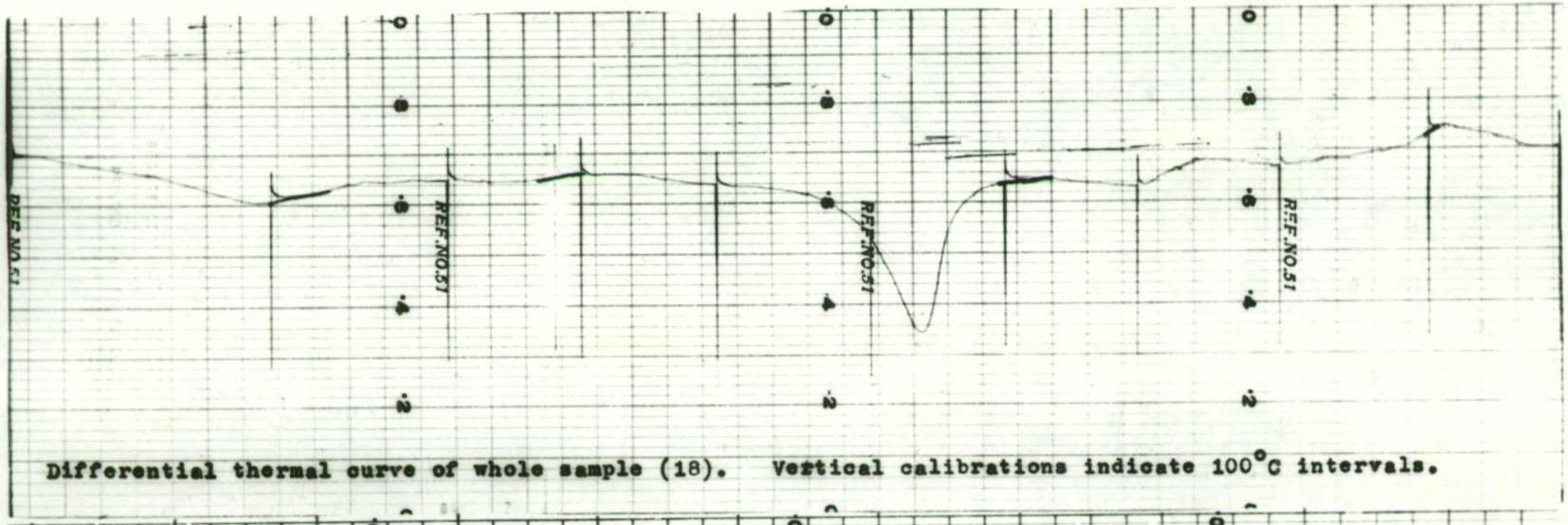
Differential thermal curve of less than 2 microns fraction (16). Vertical calibrations indicate 100°C intervals.



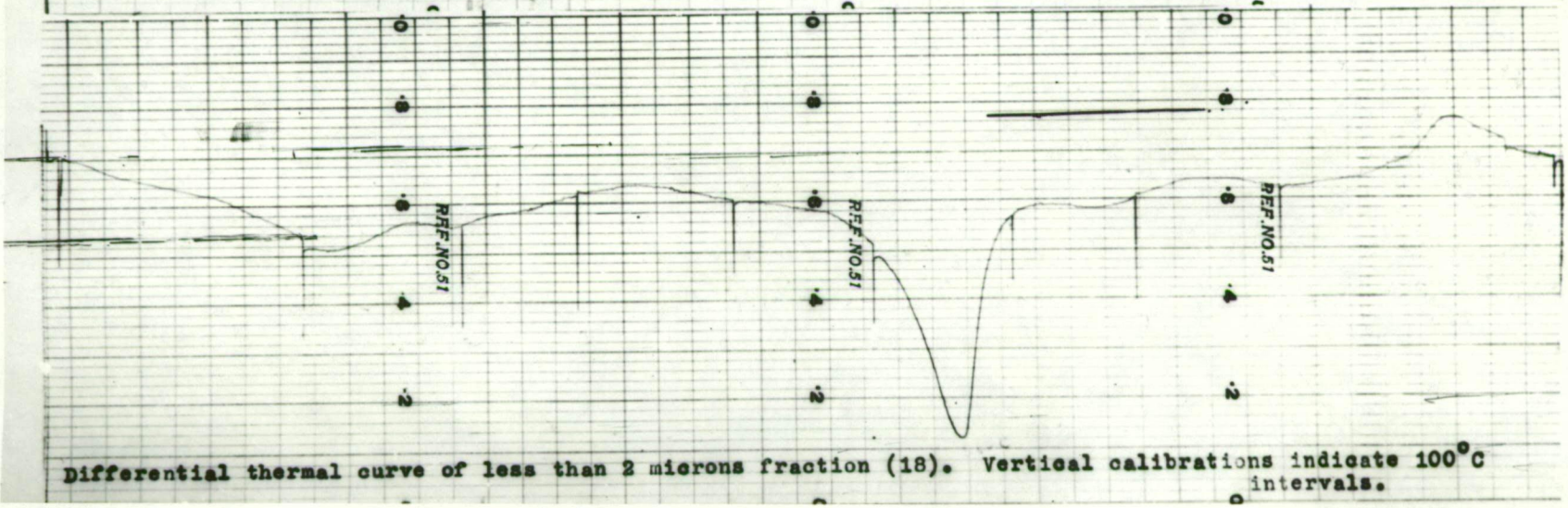
Differential thermal curve of whole sample (17). Vertical calibrations indicate 100°C intervals.



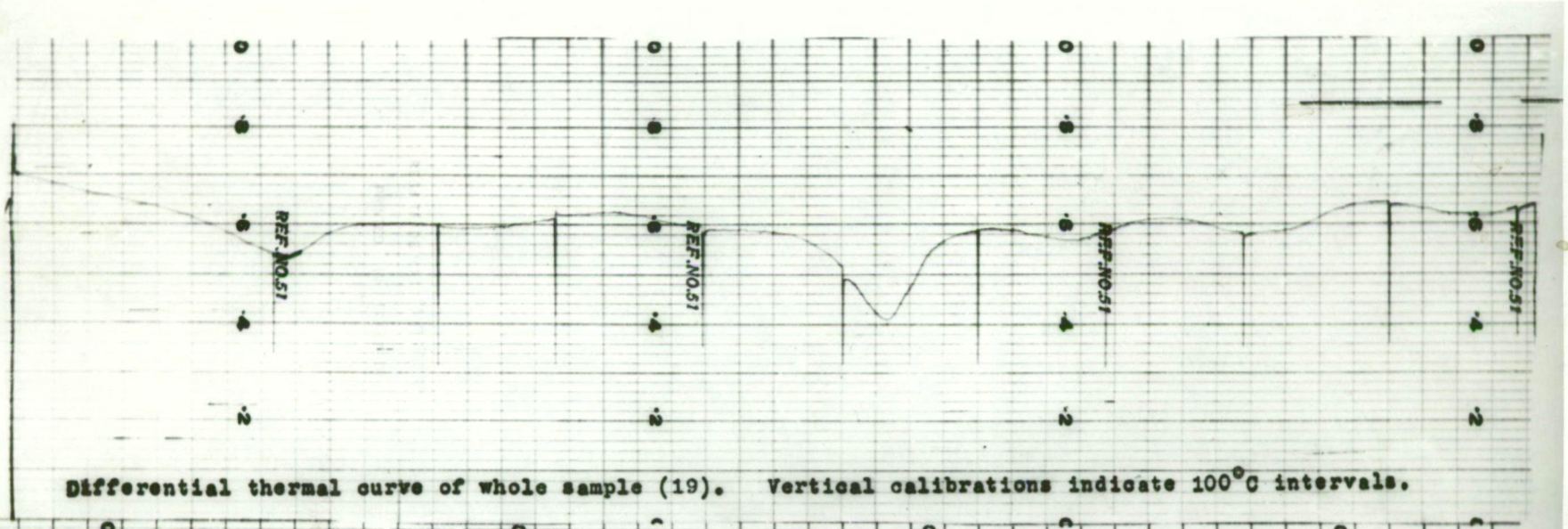
Differential thermal curve of less than 2 microns fraction (17). Vertical calibrations indicate 100°C intervals.



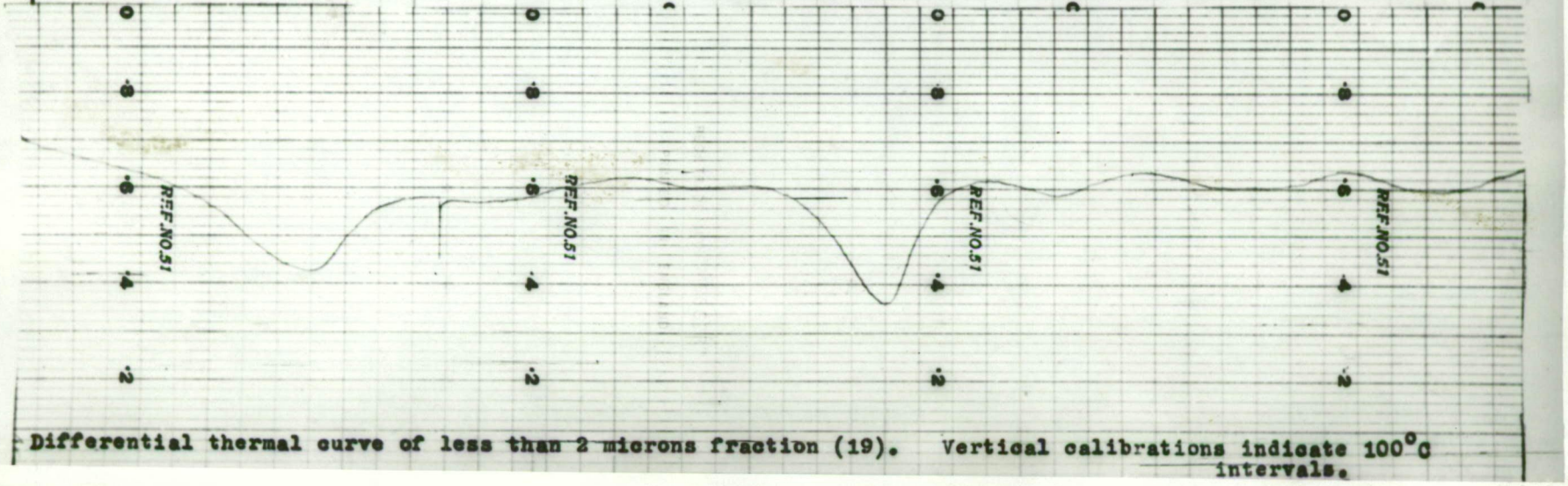
Differential thermal curve of whole sample (18). Vertical calibrations indicate 100°C intervals.



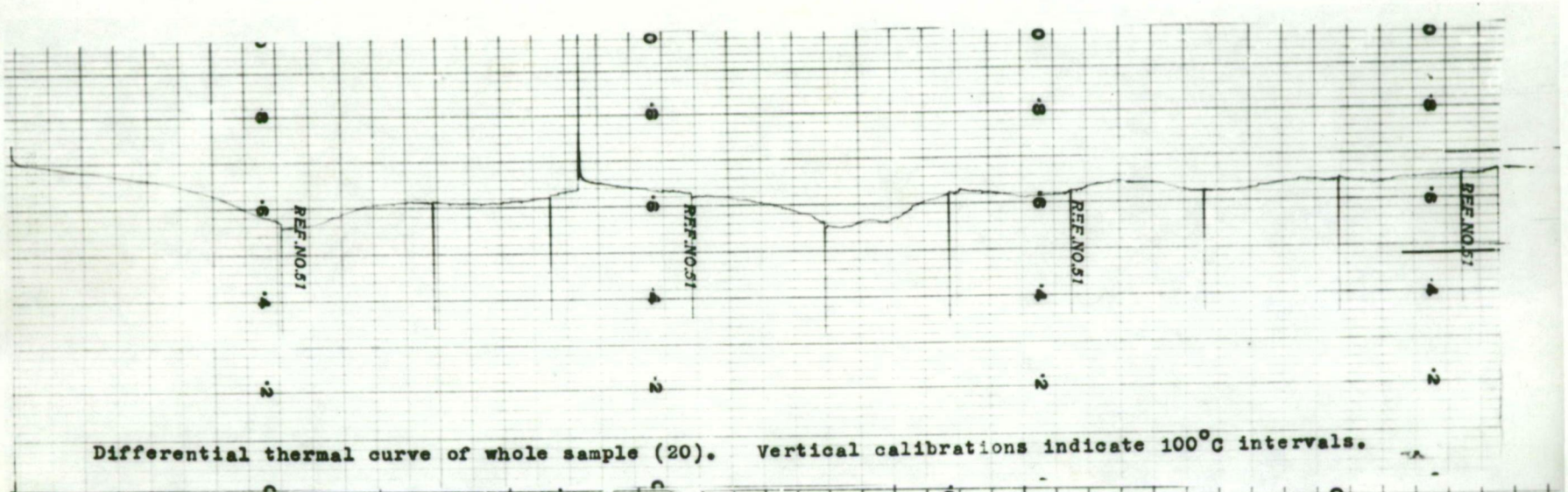
Differential thermal curve of less than 2 microns fraction (18). Vertical calibrations indicate 100°C intervals.



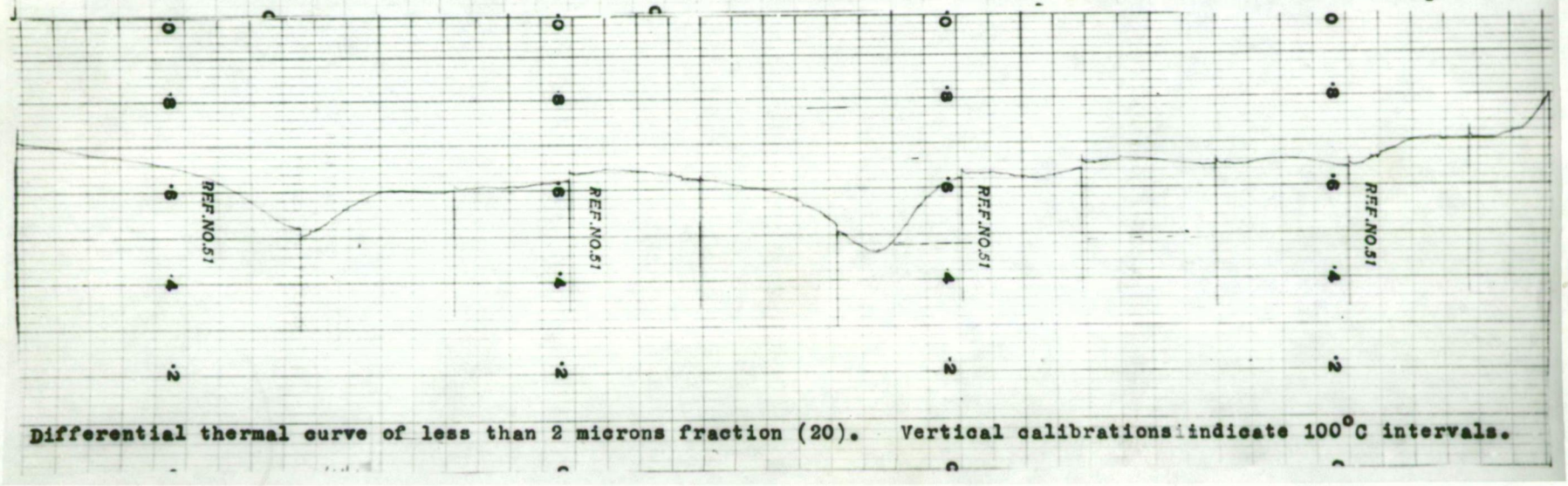
Differential thermal curve of whole sample (19). Vertical calibrations indicate 100°C intervals.



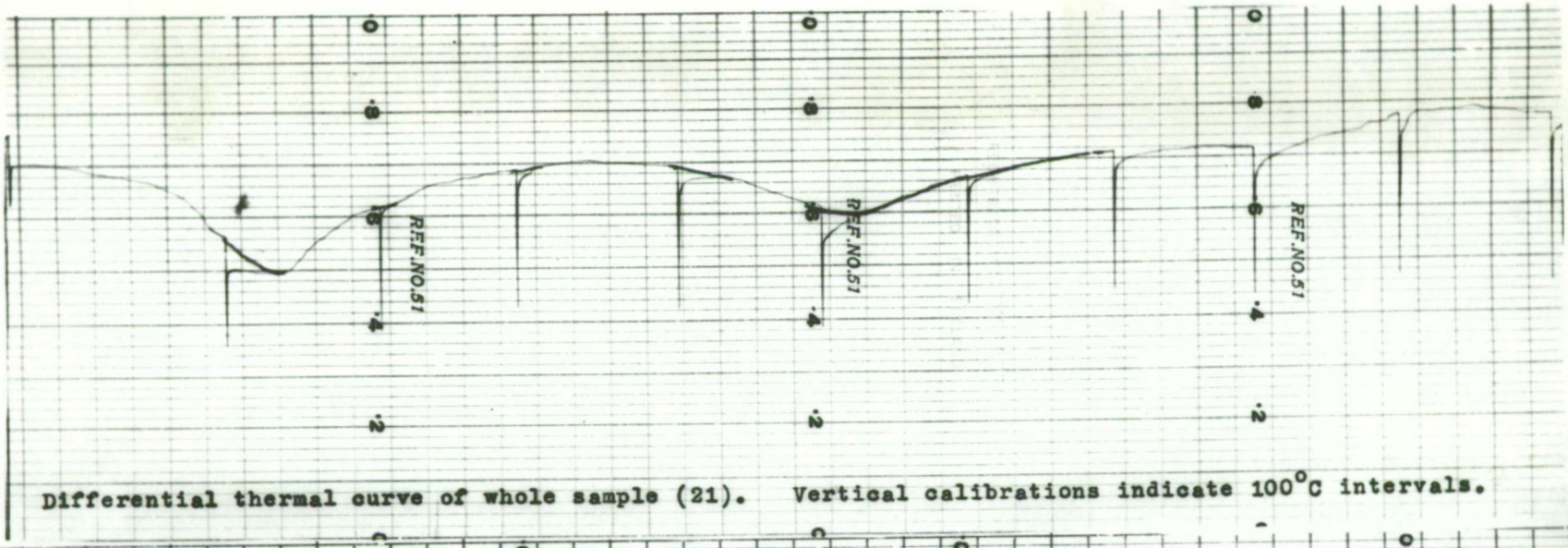
Differential thermal curve of less than 2 microns fraction (19). Vertical calibrations indicate 100°C intervals.



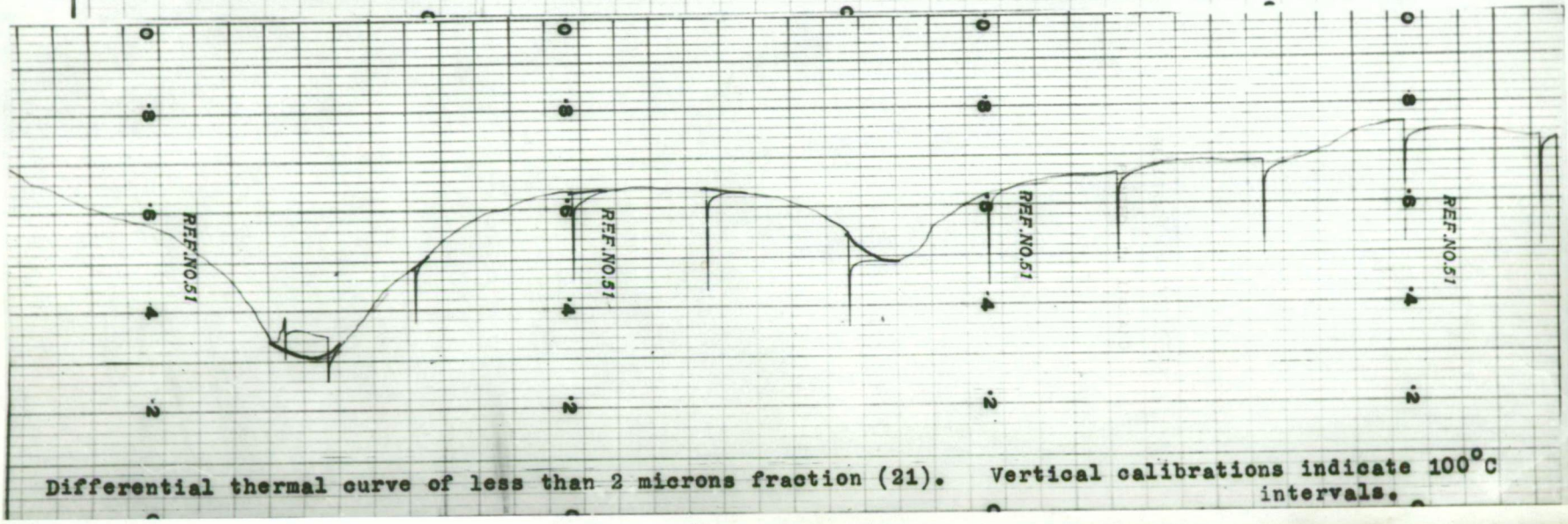
Differential thermal curve of whole sample (20). Vertical calibrations indicate 100°C intervals.



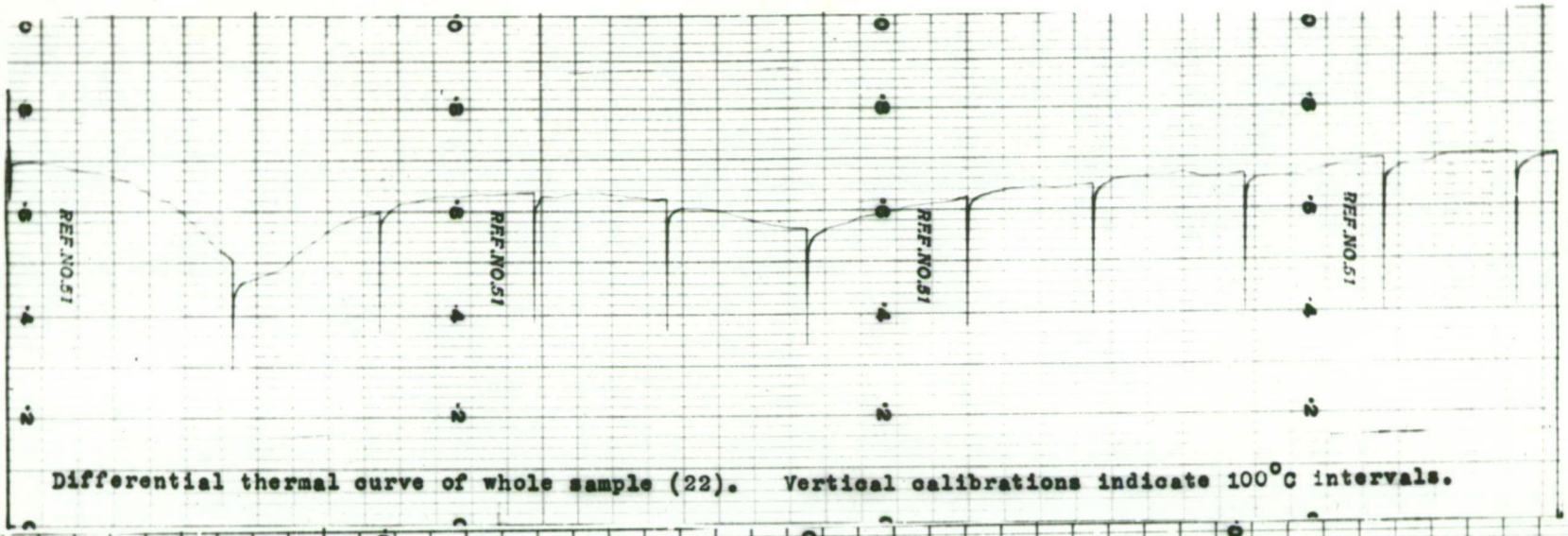
Differential thermal curve of less than 2 microns fraction (20). Vertical calibrations indicate 100°C intervals.



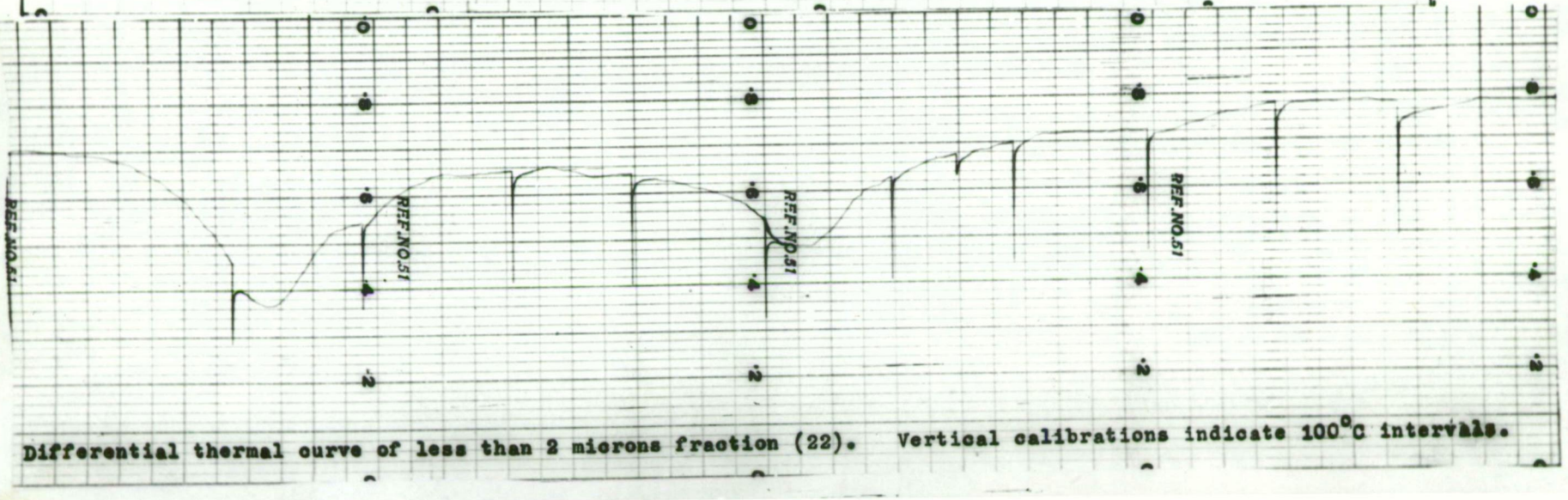
Differential thermal curve of whole sample (21). Vertical calibrations indicate 100°C intervals.



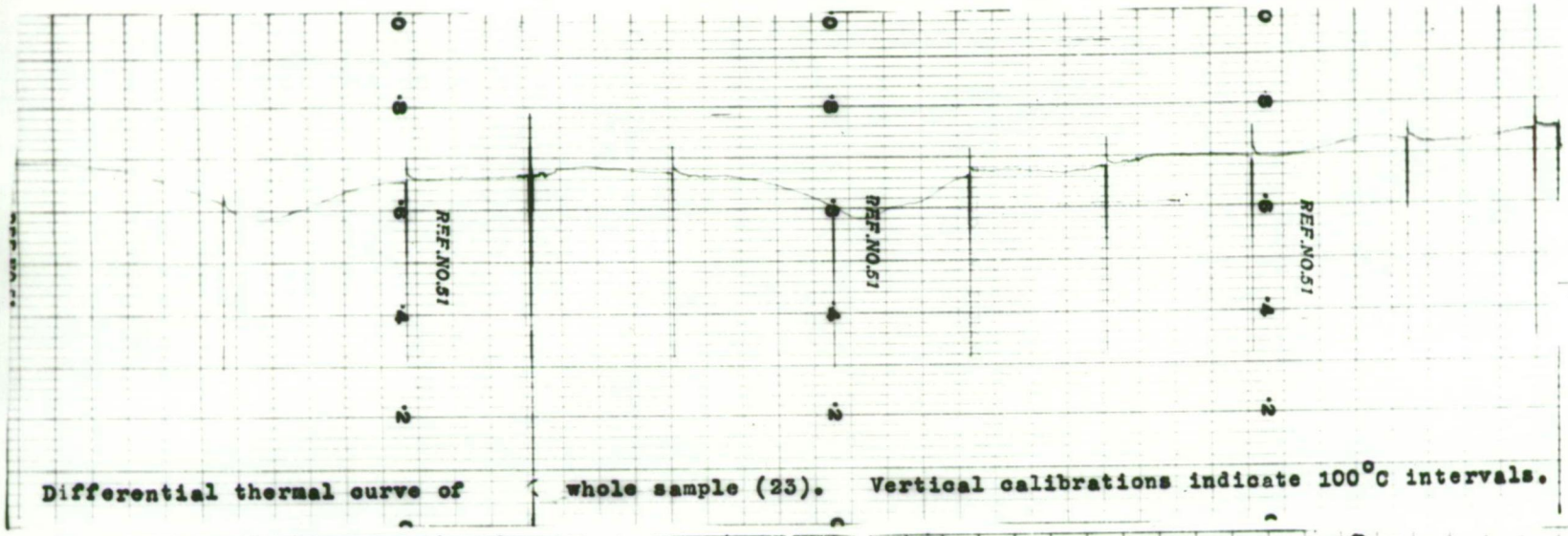
Differential thermal curve of less than 2 microns fraction (21). Vertical calibrations indicate 100°C intervals.



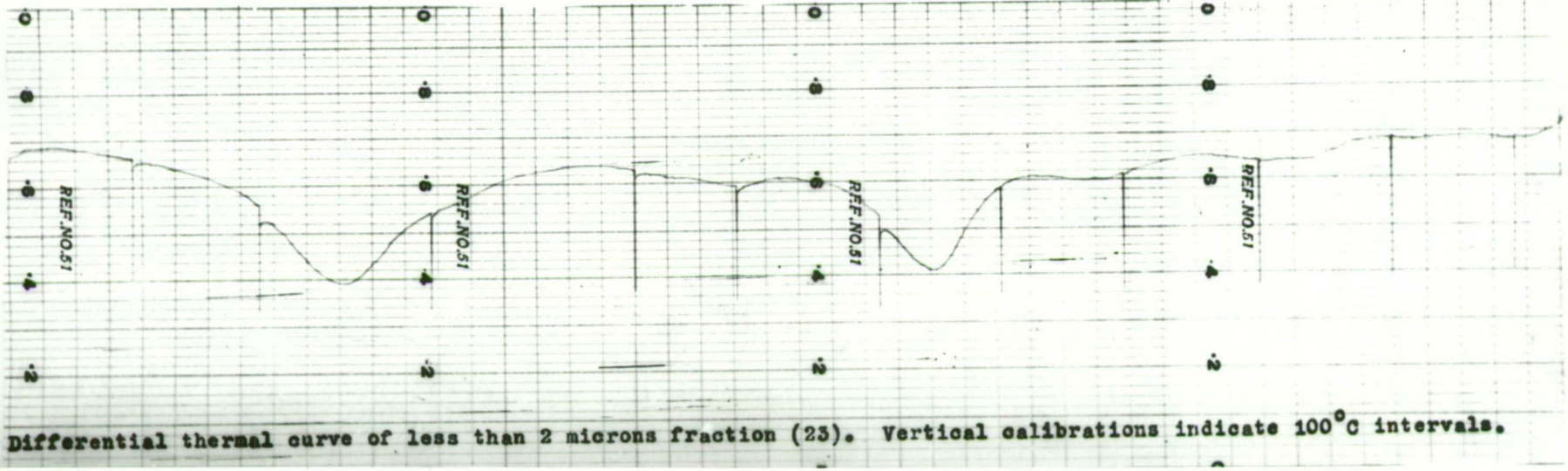
Differential thermal curve of whole sample (22). Vertical calibrations indicate 100°C intervals.



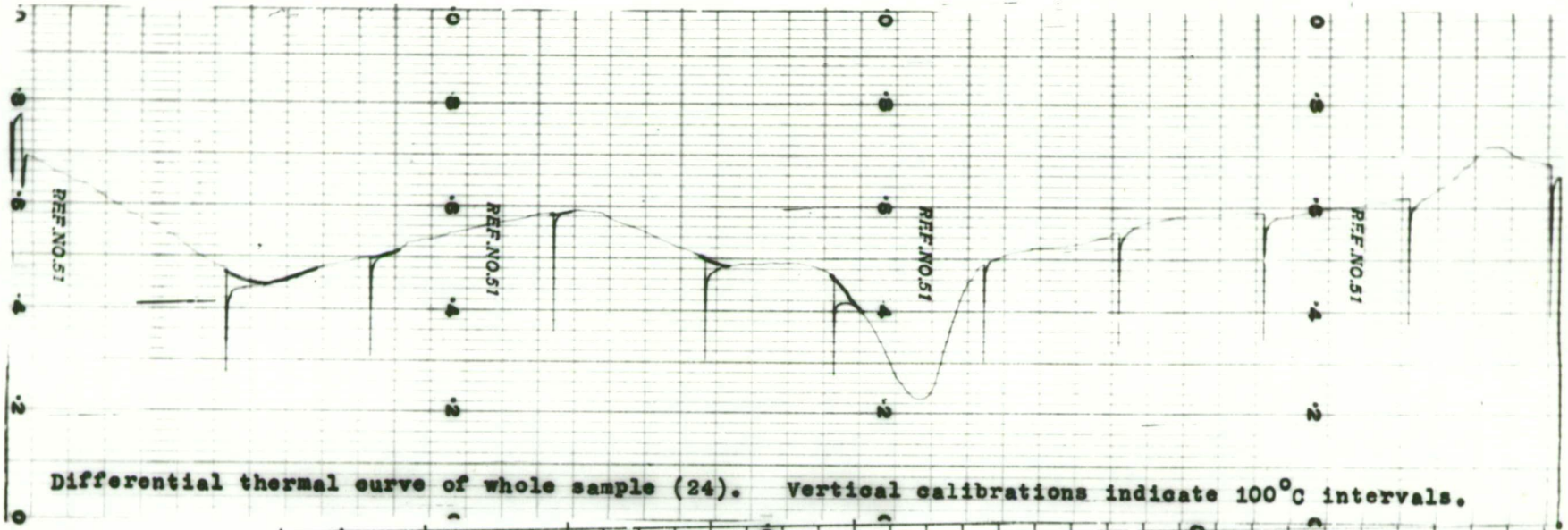
Differential thermal curve of less than 2 microns fraction (22). Vertical calibrations indicate 100°C intervals.



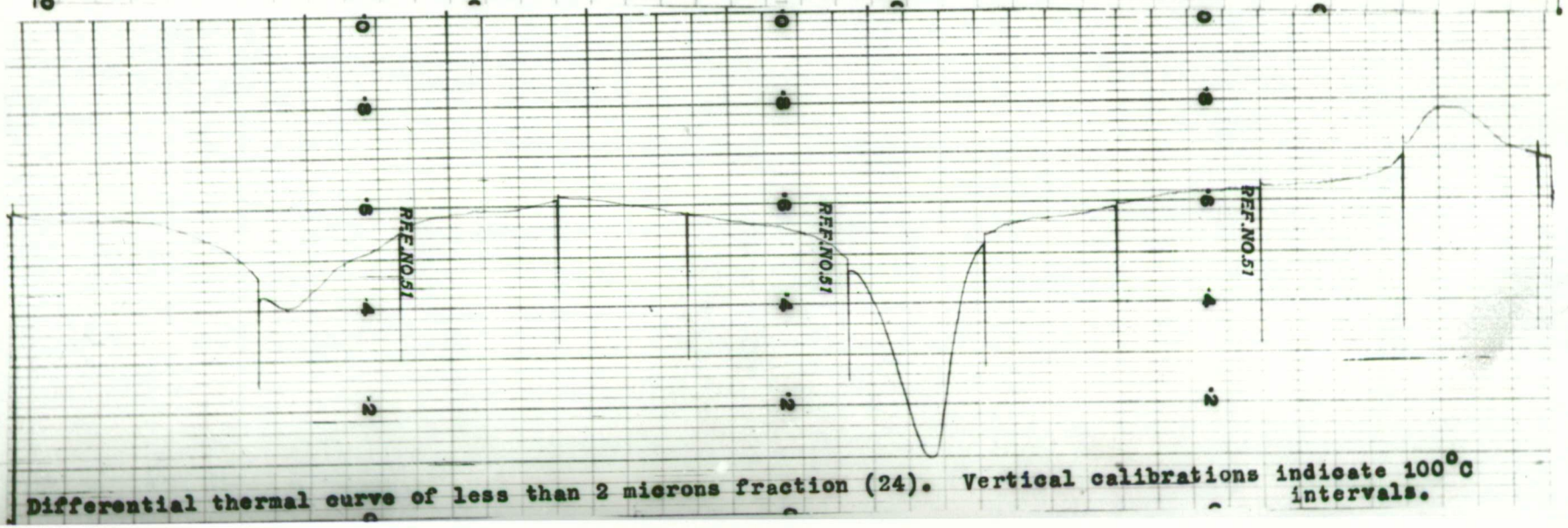
Differential thermal curve of whole sample (23). Vertical calibrations indicate 100°C intervals.



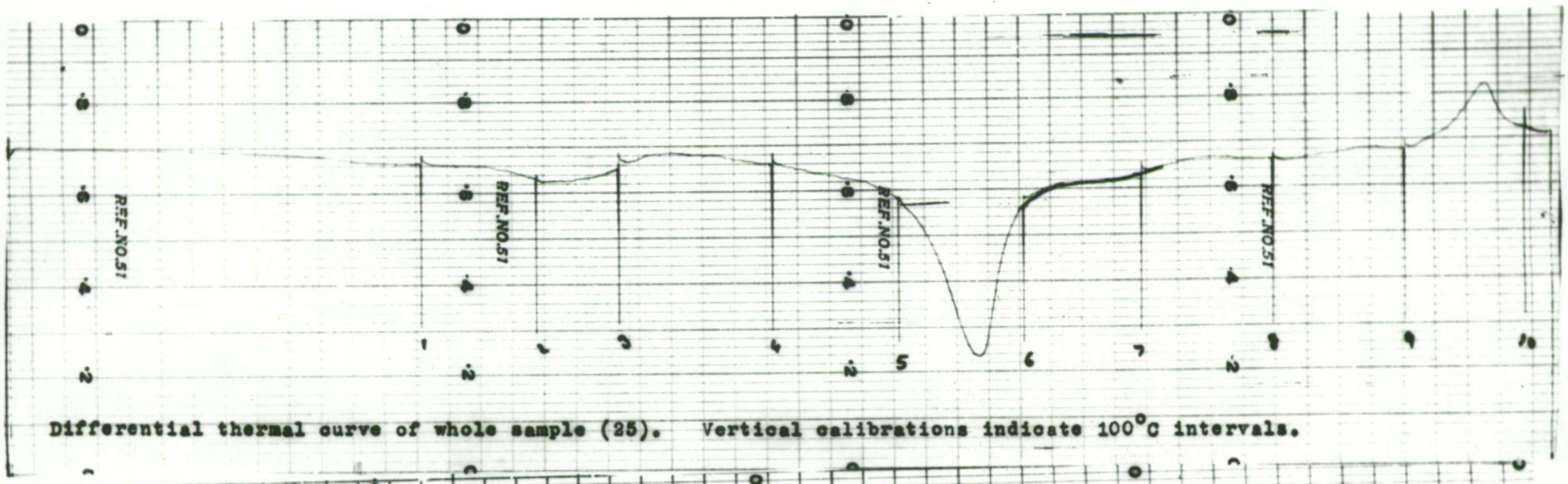
Differential thermal curve of less than 2 microns fraction (23). Vertical calibrations indicate 100°C intervals.



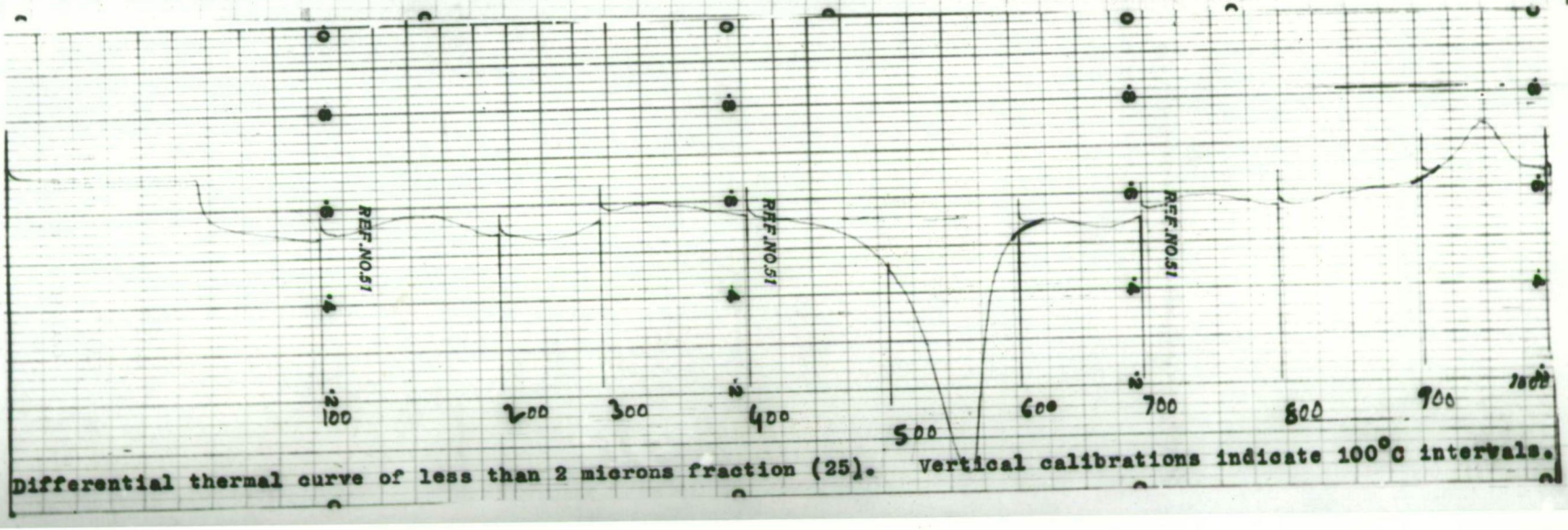
Differential thermal curve of whole sample (24). Vertical calibrations indicate 100°C intervals.



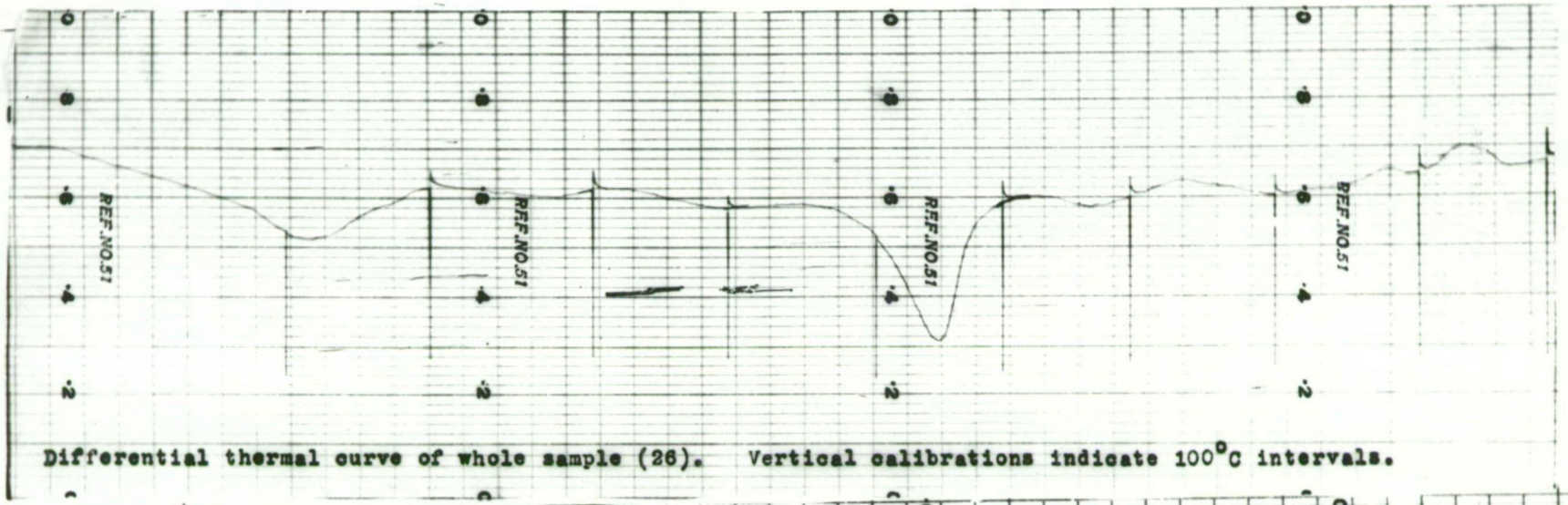
Differential thermal curve of less than 2 microns fraction (24). Vertical calibrations indicate 100°C intervals.



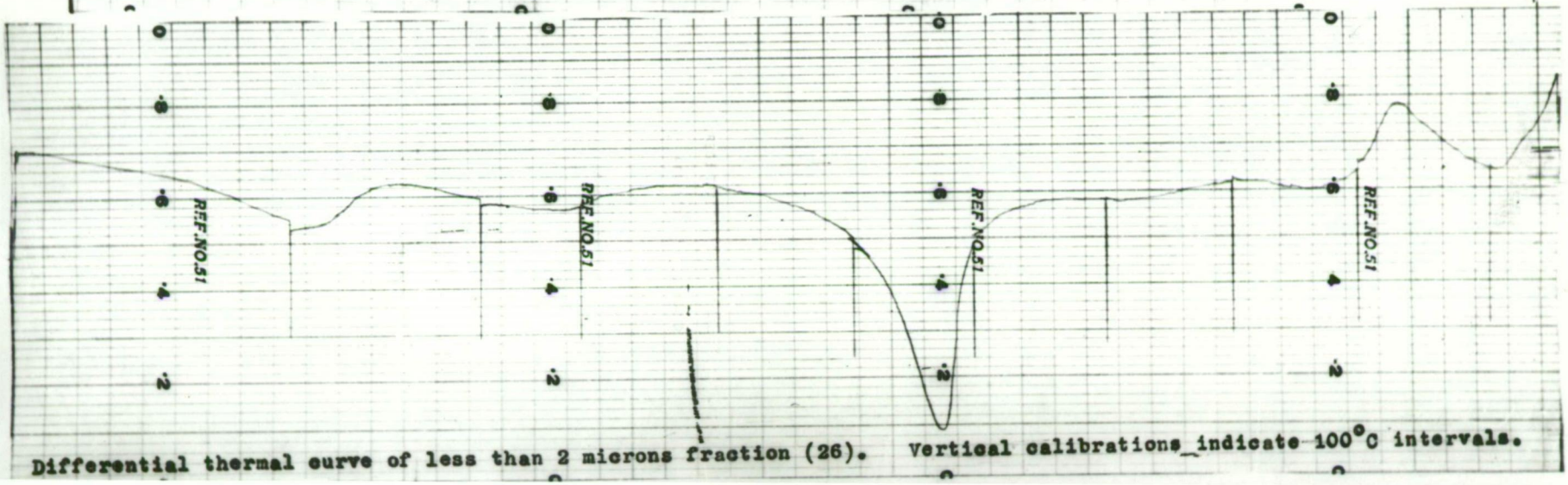
Differential thermal curve of whole sample (25). Vertical calibrations indicate 100°C intervals.



Differential thermal curve of less than 2 microns fraction (25). Vertical calibrations indicate 100°C intervals.

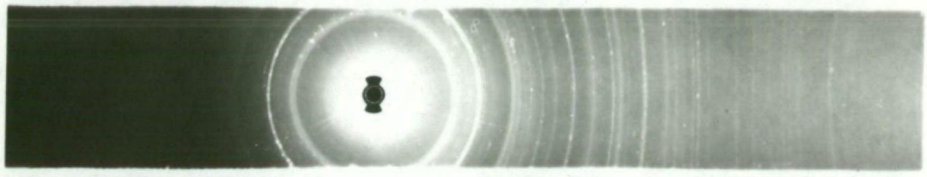


Differential thermal curve of whole sample (26). Vertical calibrations indicate 100°C intervals.

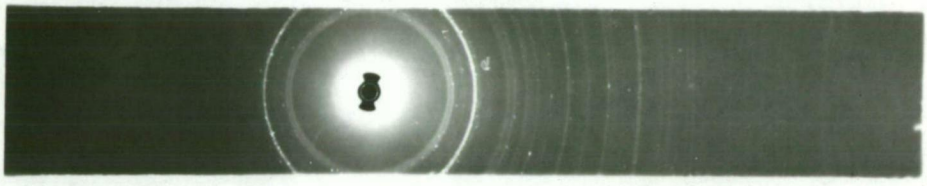


Differential thermal curve of less than 2 microns fraction (26). Vertical calibrations indicate 100°C intervals.

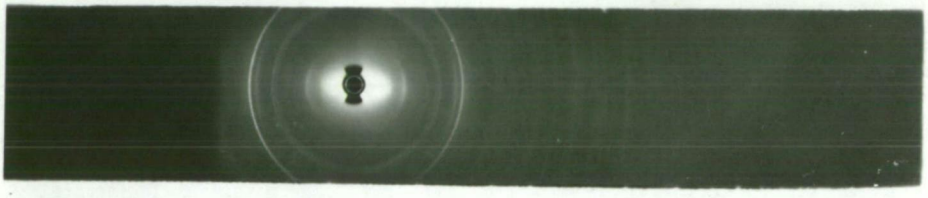
Whole sample (1) untreated



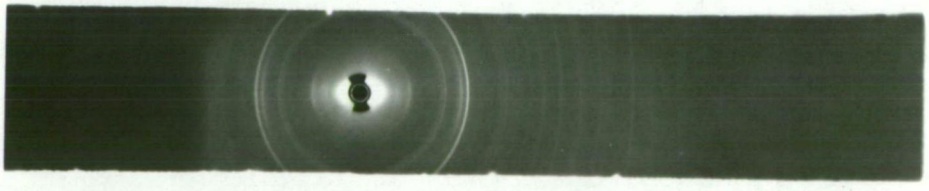
Whole sample (1) +glycerol



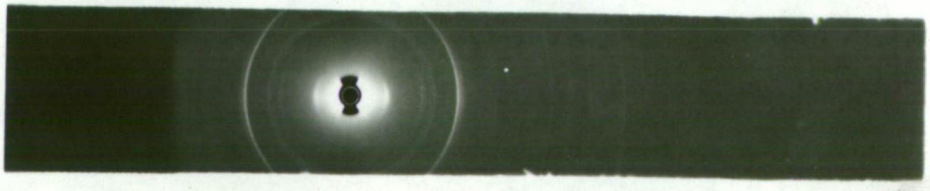
Whole sample (1) heated to 600°C



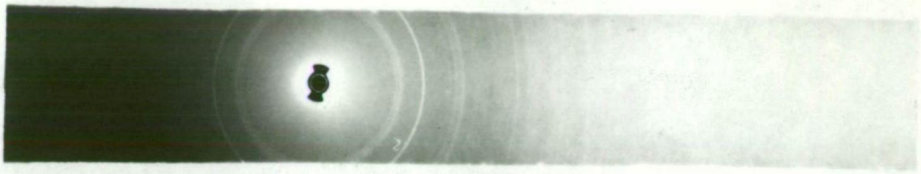
Aggregate less than 2 microns untreated



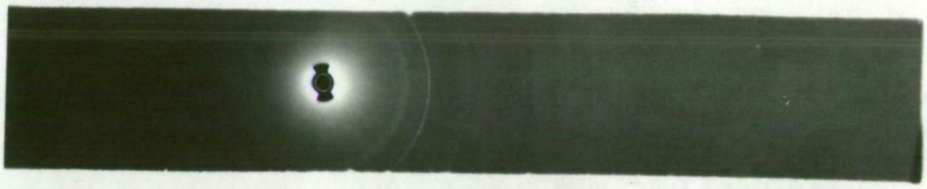
Aggregate less than 2 microns + glycerol



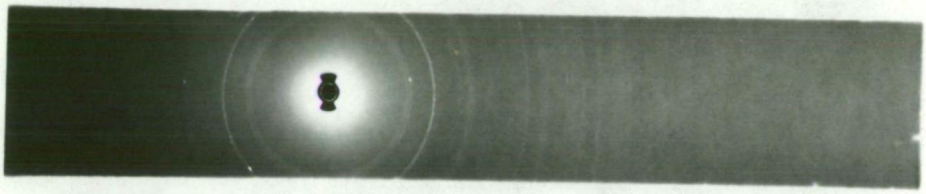
Aggregate less than 2 microns heated to 600°C



Whole sample (1A) untreated

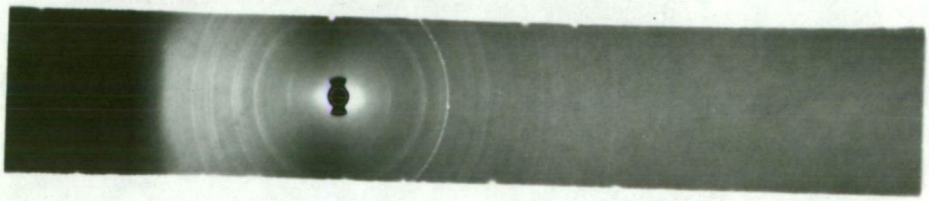


Whole sample (1A) + glycerol



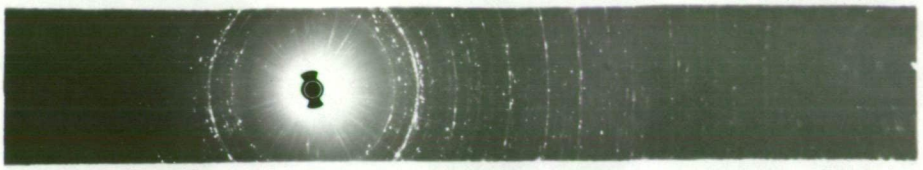
Whole sample (1A) heated to 600°C

Aggregate less than 2 microns untreated



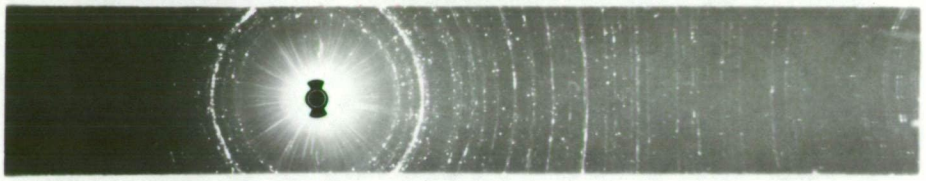
Aggregate less than 2 microns + glycerol

Aggregate less than 2 microns heated to 600°C

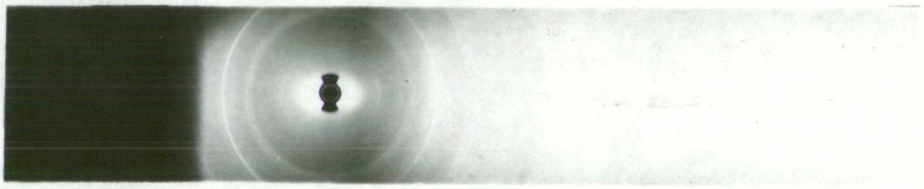


Whole sample (2) untreated

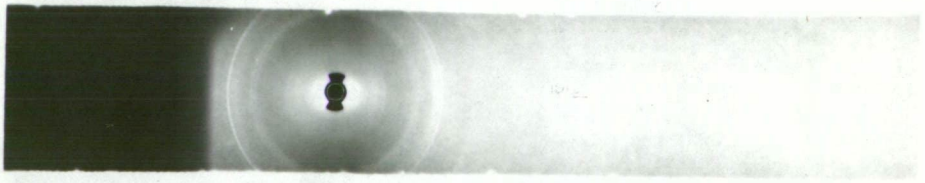
Whole sample (2) + glycerol



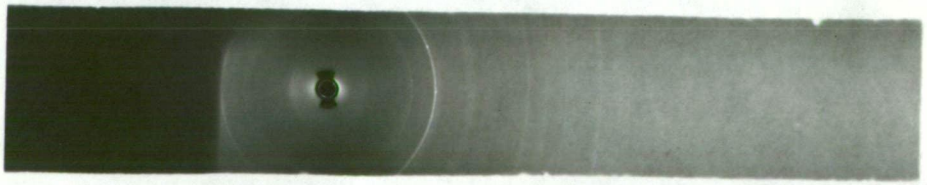
Whole sample (2) heated to 600°C



Aggregate less than 2 microns untreated

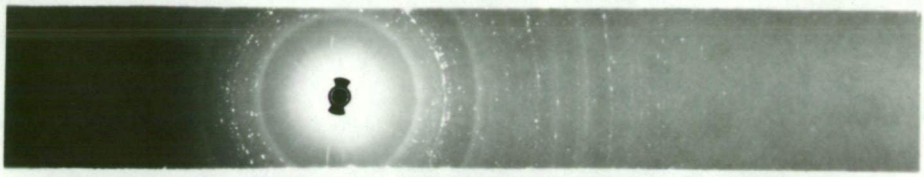


Aggregate less than 2 microns + glycerol

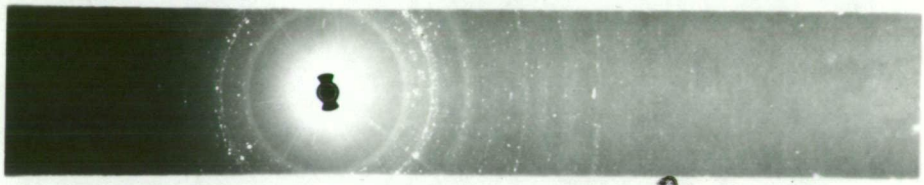


Aggregate less than 2 microns heated to 600°C

Whole sample (3) untreated

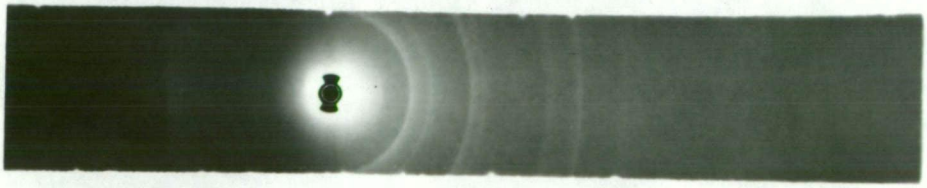


Whole sample (3) + glycerol



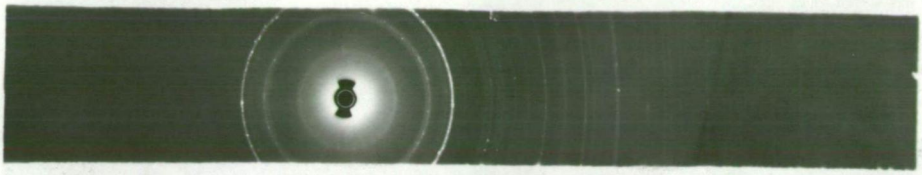
Whole sample (3) heated to 600°C

Aggregate less than 2 microns untreated

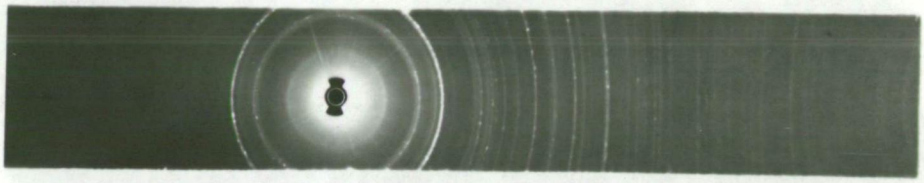


Aggregate less than 2 microns + glycerol

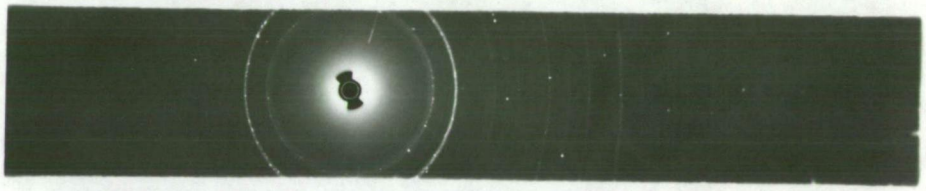
Aggregate less than 2 microns heated to 600°C



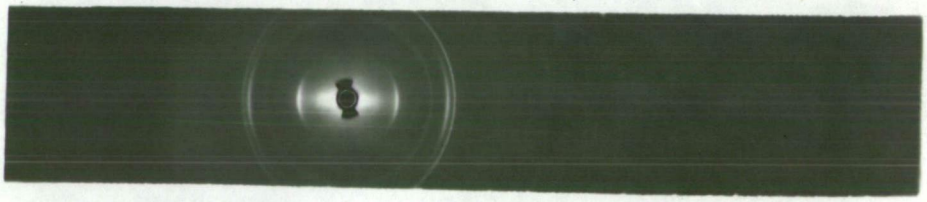
Whole sample (4) untreated



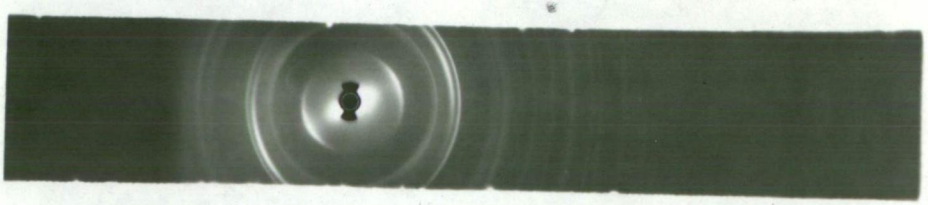
Whole sample (4) + glycerol



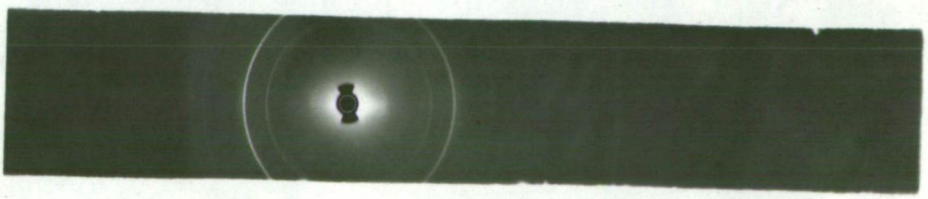
Whole sample (4) heated to 600°C



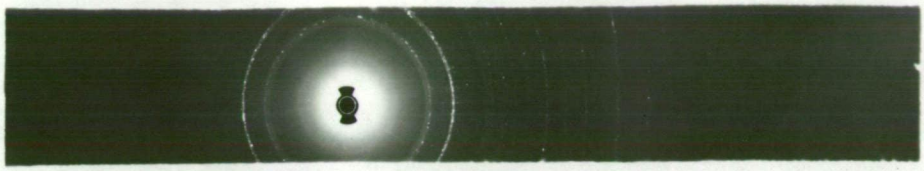
Aggregate less than 2 microns untreated



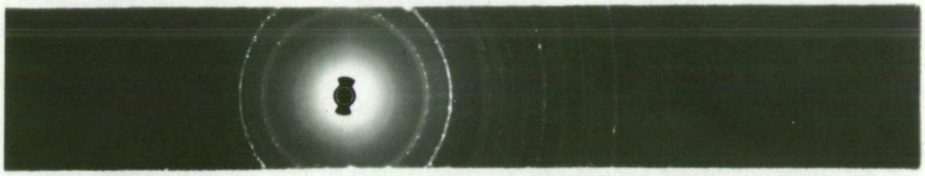
Aggregate less than 2 microns + glycerol



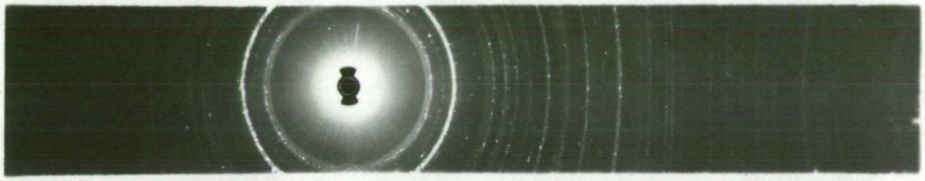
Aggregate less than 2 microns heated to 600°C



Whole sample (5) untreated

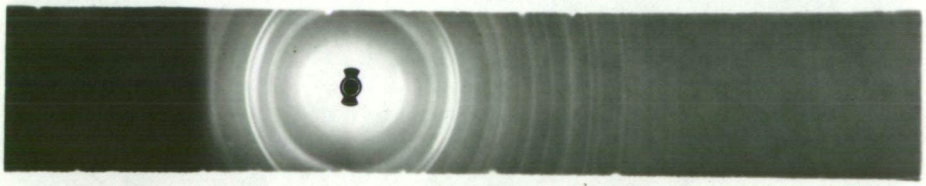


Whole sample (5) + glycerol



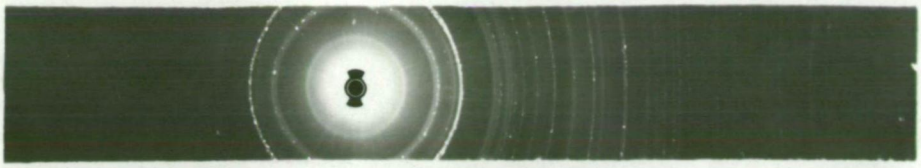
Whole sample (5) heated to 600°C

Aggregate less than 2 microns untreated

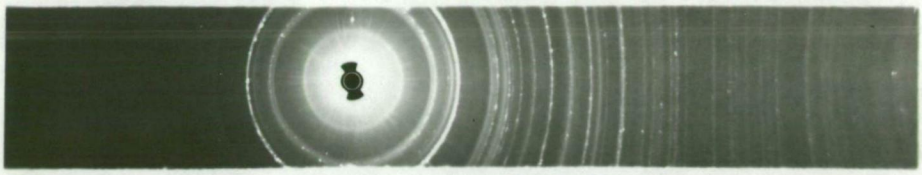


Aggregate less than 2 microns + glycerol

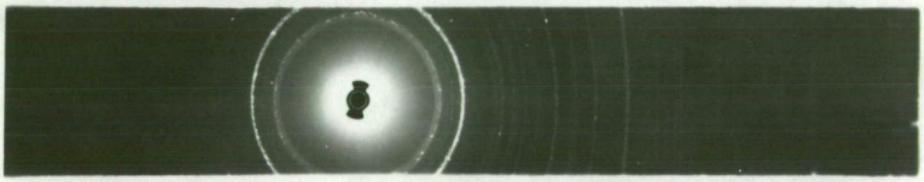
Aggregate less than 2 microns heated to 600°C



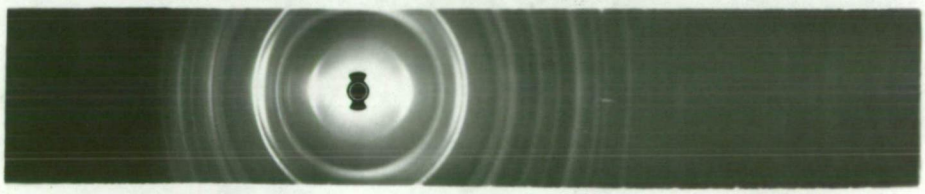
Whole sample (6) untreated



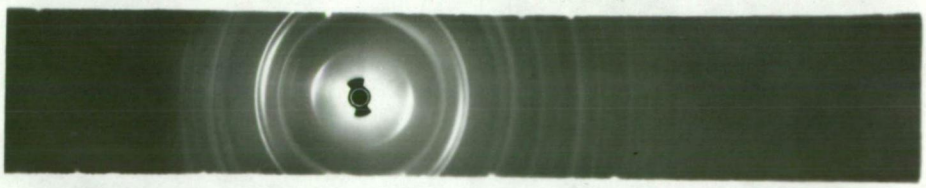
Whole sample (6) + glycerol



Whole sample (6) heated to 600°C

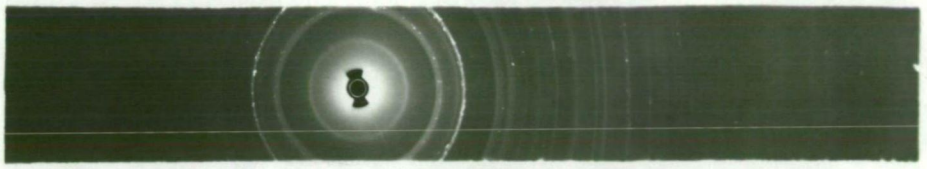


Aggregate less than 2 microns untreated



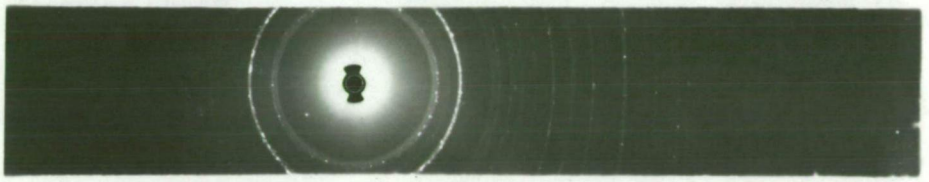
Aggregate less than 2 microns + glycerol

Aggregate less than 2 microns heated to 600°C

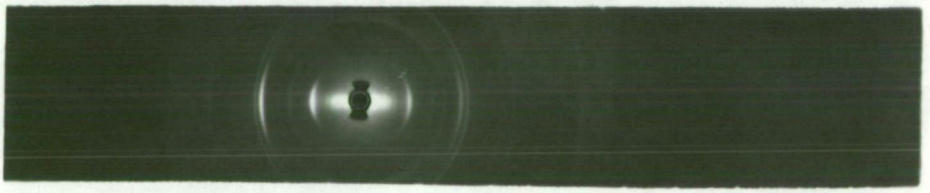


Whole sample (7) untreated

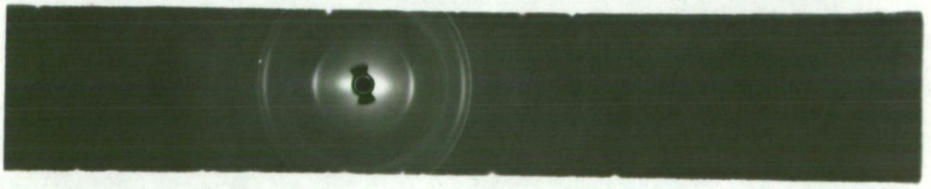
Whole sample (7) + glycerol



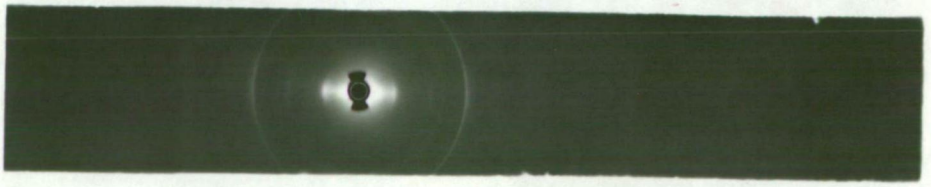
Whole sample (7) heated to 600°C



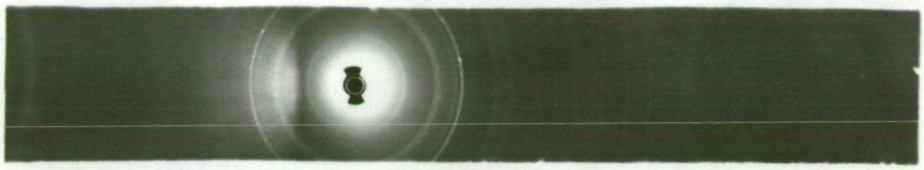
Aggregate less than 2 microns untreated



Aggregate less than 2 microns + glycerol

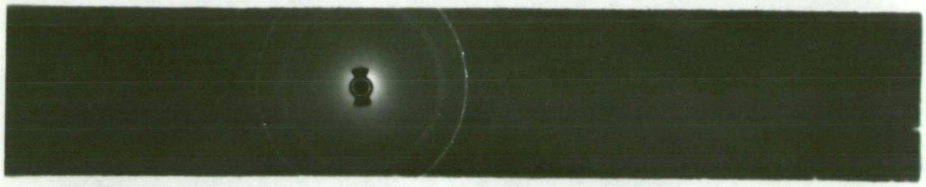


Aggregate less than 2 microns heated to 600°C

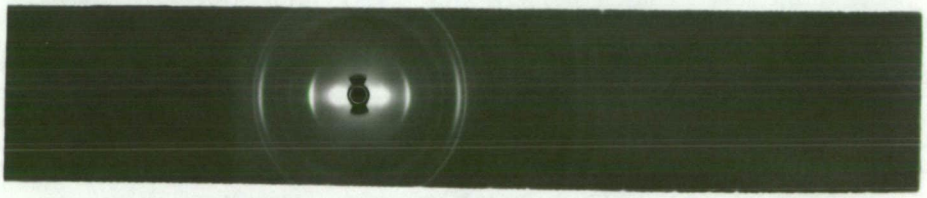


Whole sample (8) untreated

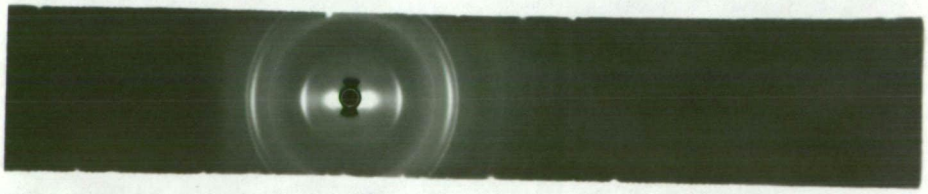
Whole sample (8) + glycerol



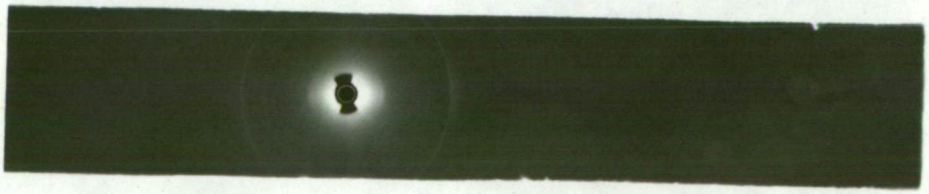
Whole sample (8) heated to 600°C



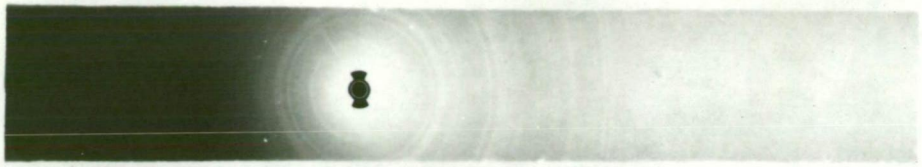
Aggregate less than 2 microns untreated



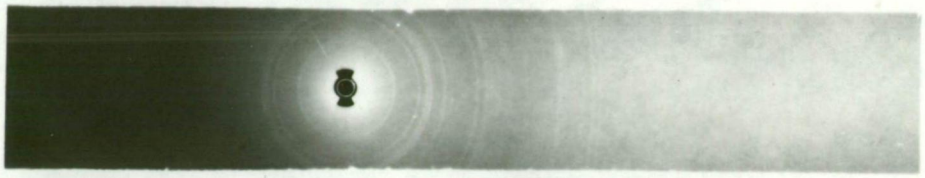
Aggregate less than 2 microns + glycerol



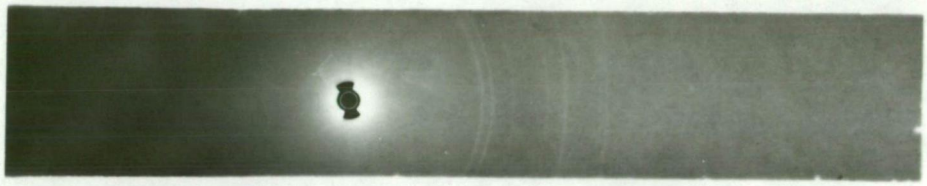
Aggregate less than 2 microns heated to 600°C



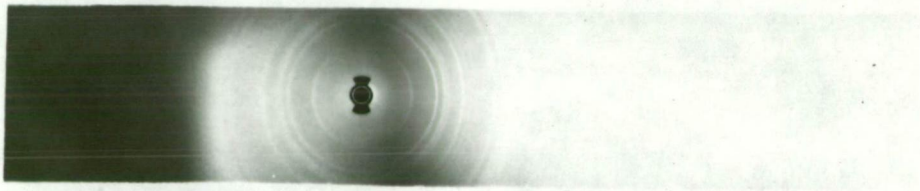
Whole sample (9) untreated



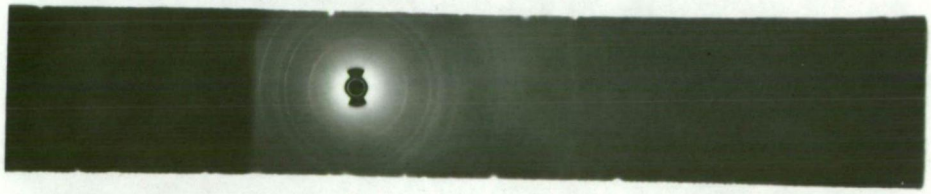
Whole sample (9) + glycerol



Whole sample (9) heated to 600°C



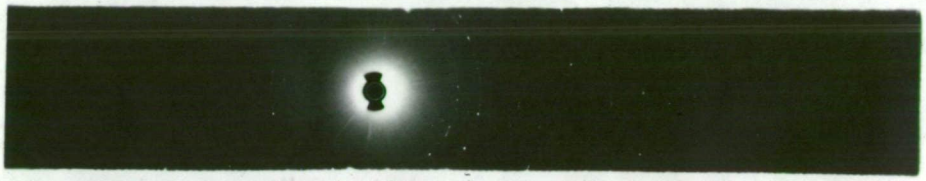
Aggeregate less than 2 microns untreated



Aggregate less than 2 microns + glycerol

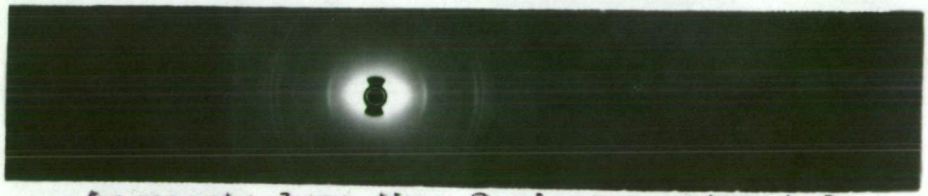
Aggregate less than 2 microns heated to 600°C

Whole sample (10) untreated

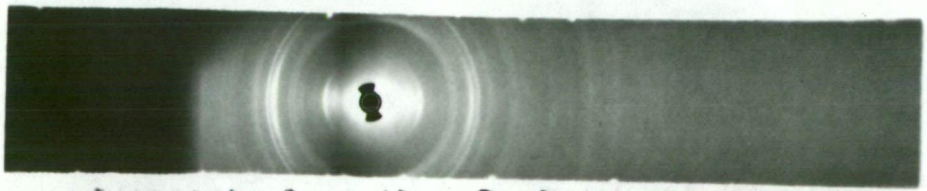


Whole sample (10) +glycerol

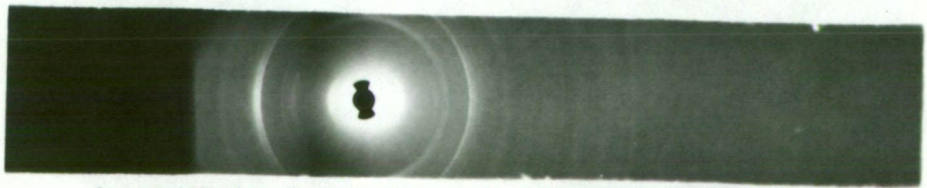
Whole sample (10) heated to 600°C



Aggregate less than 2 microns untreated

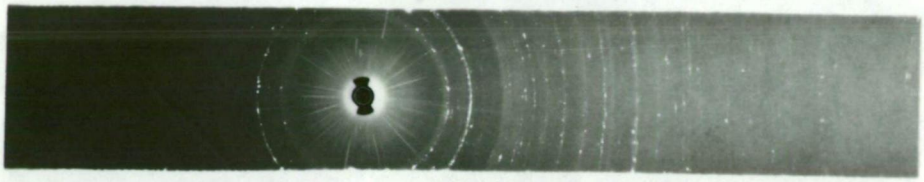


Aggregate less than 2 microns + glycerol

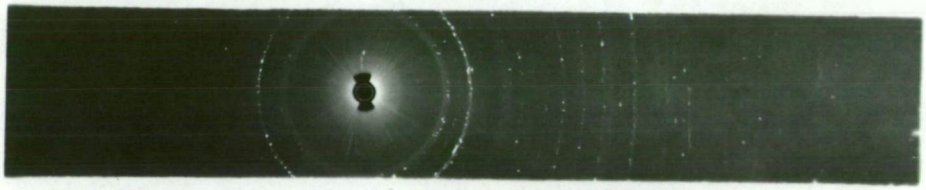


Aggregate less than 2 microns heated to 600°C

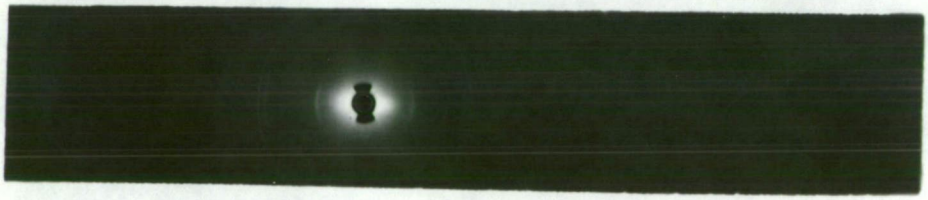
Whole sample (11) untreated



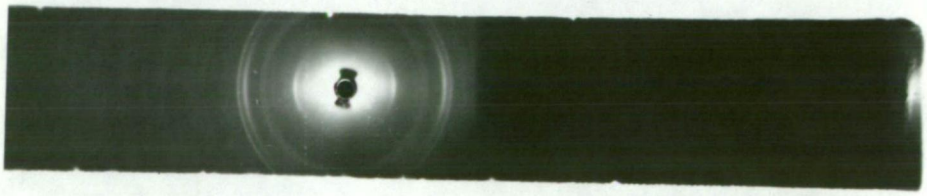
Whole sample (11) + glycerol



Whole sample (11) heated to 600°C



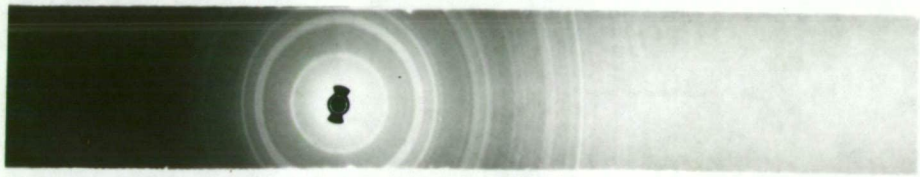
Aggregate less than 2 microns untreated



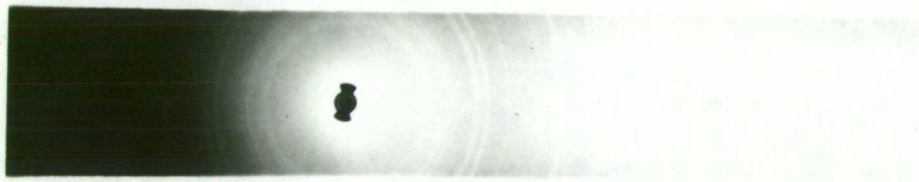
Aggregate less than 2 microns + glycerol

Aggregate less than 2 microns heated to 600°C

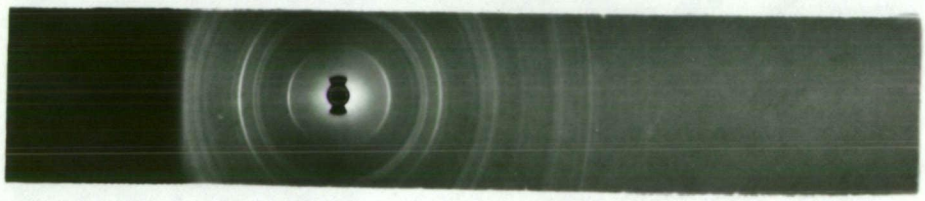
Whole sample (12) untreated



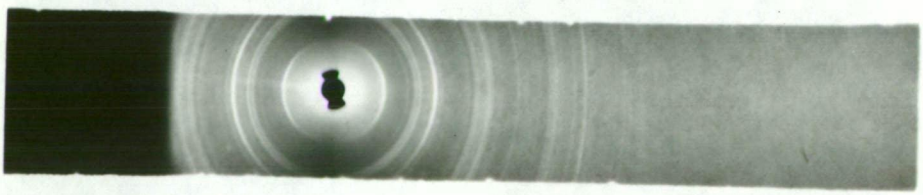
Whole sample (12) + glycerol



Whole sample (12) heated to 600°C

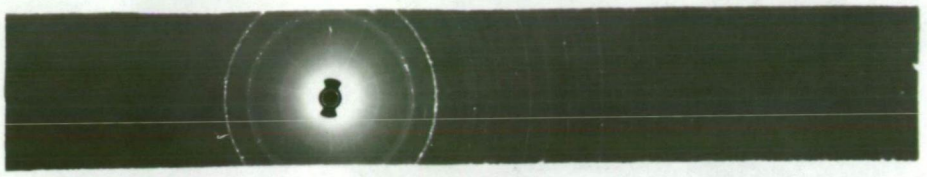


Aggregate less than 2 microns untreated

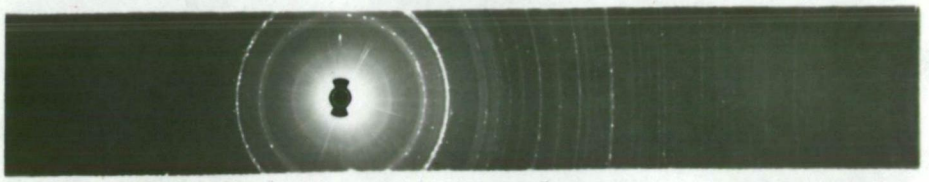


Aggregate less than 2 microns + glycerol

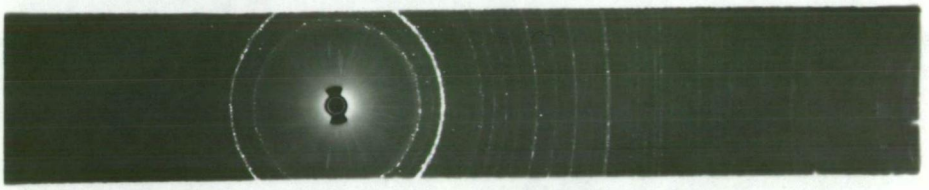
Aggregate less than 2 microns heated to 600°C



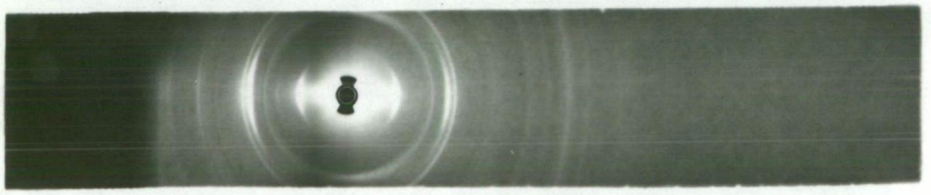
Whole sample (13) untreated



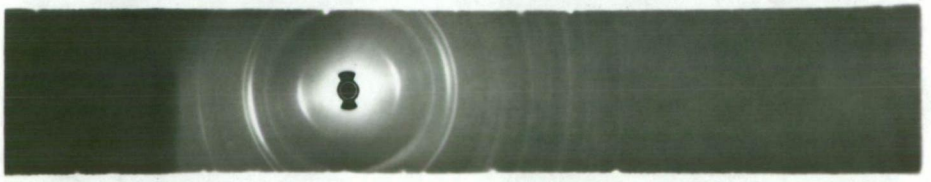
Whole sample (13) + glycerol



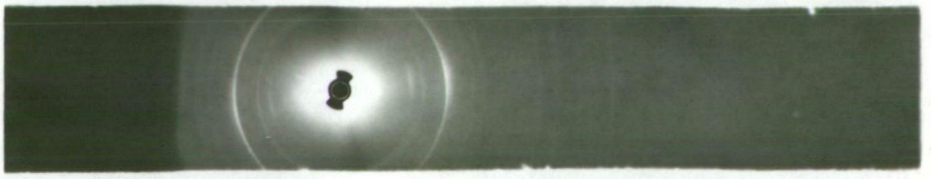
Whole sample (13) heated to 600°C



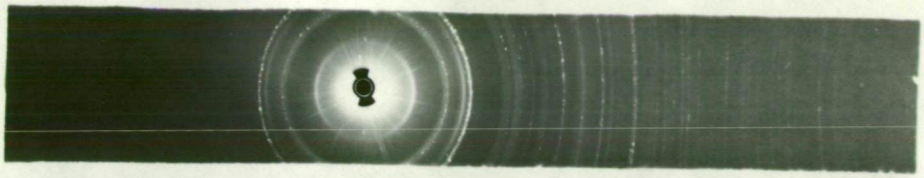
Aggregate less than 2 microns untreated



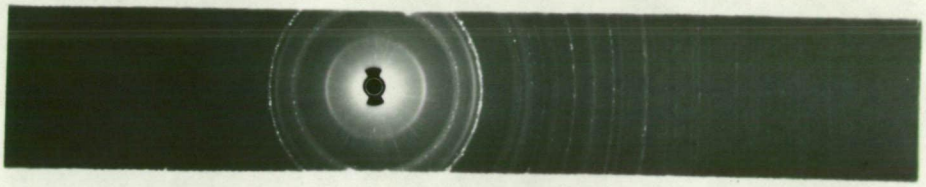
Aggregate less than 2 microns + glycerol



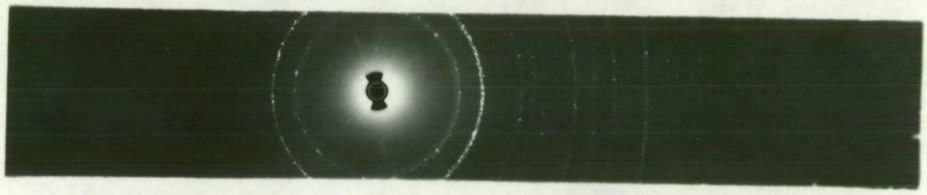
Aggregate less than 2 microns heated to 600°C



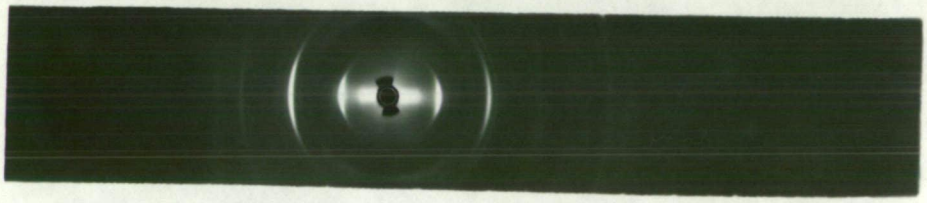
Whole sample (14) untreated



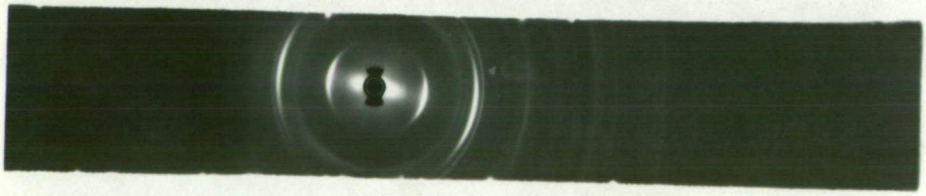
Whole sample (14) + glycerol



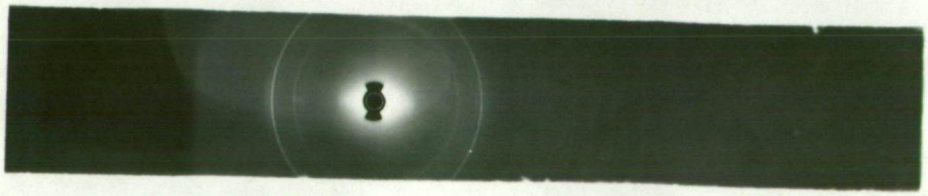
Whole sample (14) heated to 600°C



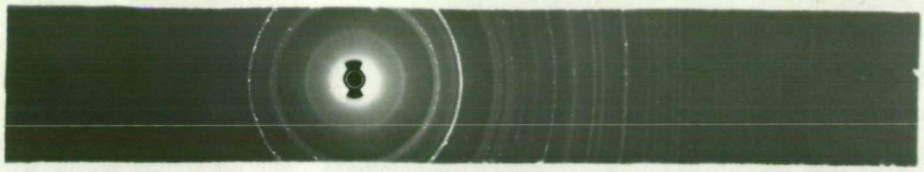
Aggregate less than 2 microns untreated



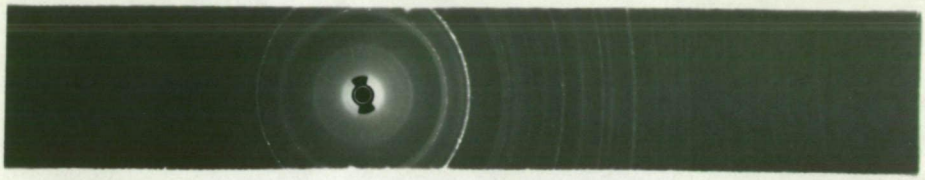
Aggregate less than 2 microns + glycerol



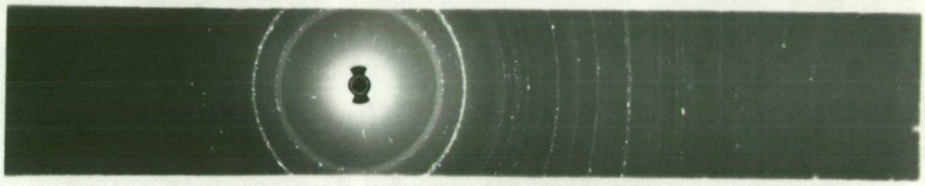
Aggregate less than 2 microns heated to 600°C



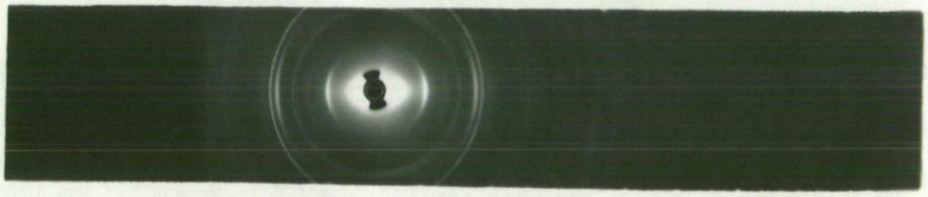
Whole sample (15) untreated



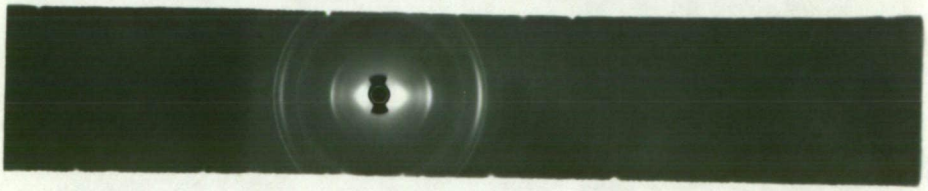
Whole sample (15) + glycerol



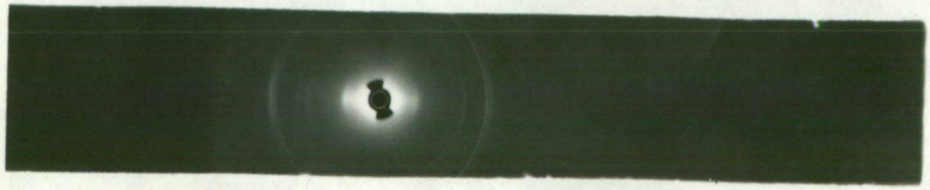
Whole sample (15) heated to 600°C



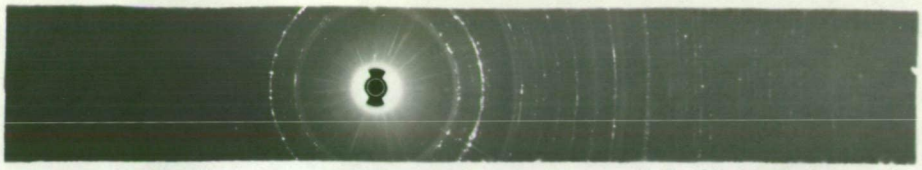
Aggregate less than 2 microns untreated



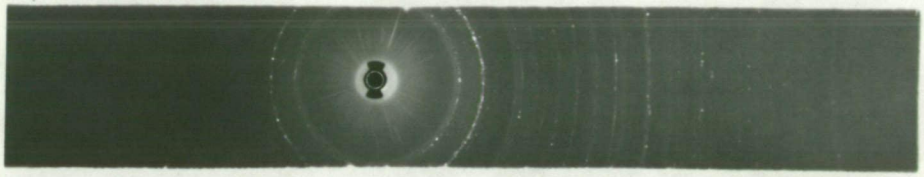
Aggregate less than 2 microns + glycerol



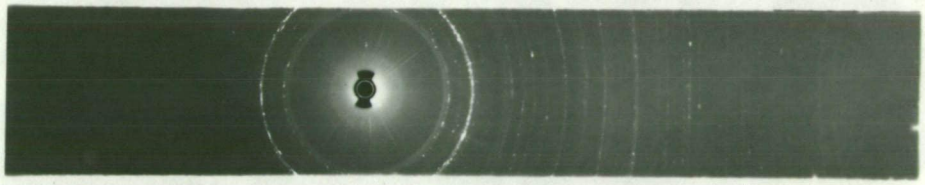
Aggregate less than 2 microns heated to 600°C



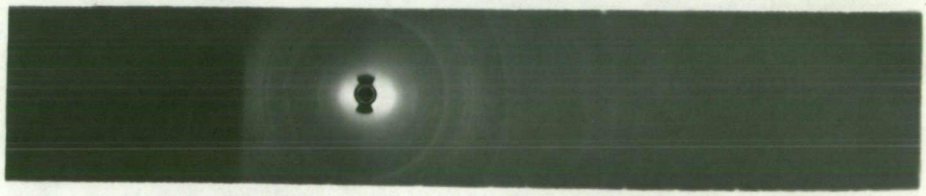
Whole sample (16) untreated



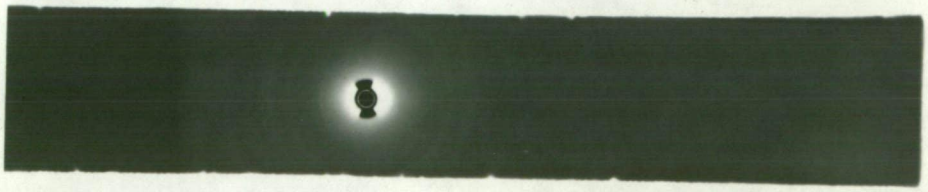
Whole sample (16) + glycerol



Whole sample (16) heated to 600°C



Aggregate less than 2 microns untreated

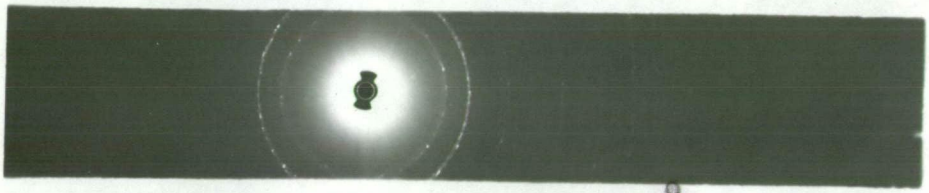


Aggregate less than 2 microns + glycerol

Aggregate less than 2 microns heated to 600°C

Whole sample (17) untreated

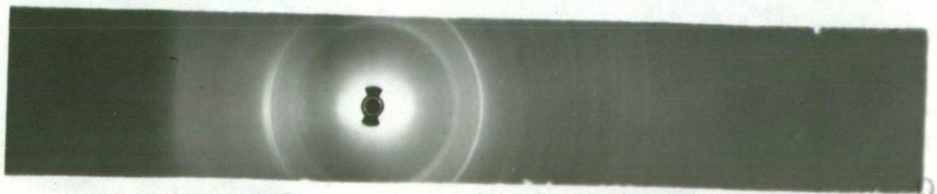
Whole sample (17) + glycerol



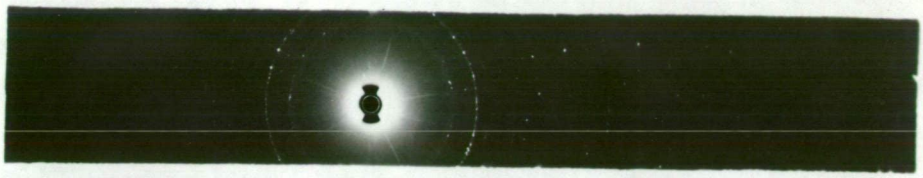
Whole sample (17) heated to 600°C

Aggregate less than 2 microns untreated

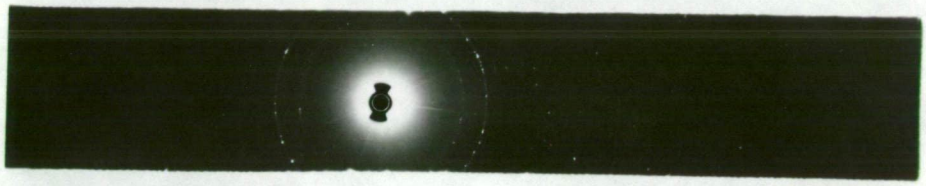
Aggregate less than 2 microns + glycerol



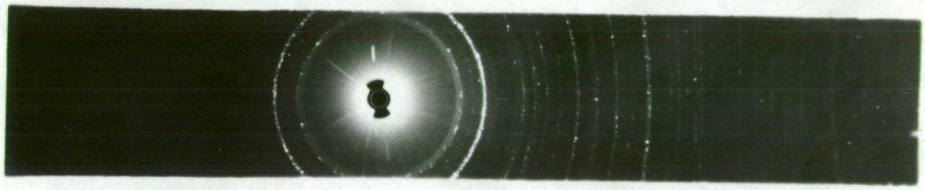
Aggregate less than 2 microns heated to 600°C



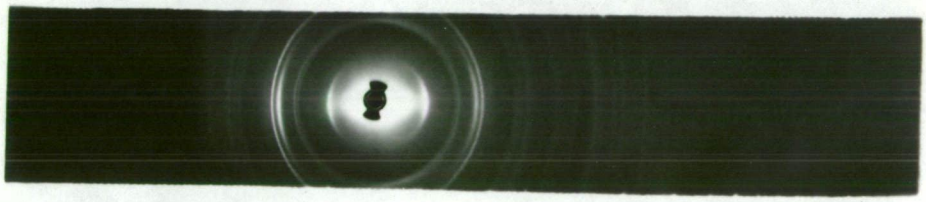
Whole sample (18) untreated



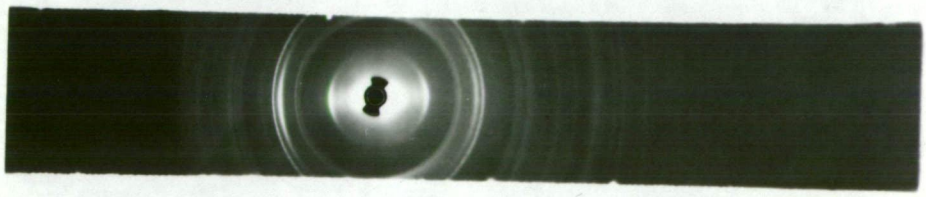
Whole sample (18) + glycerol



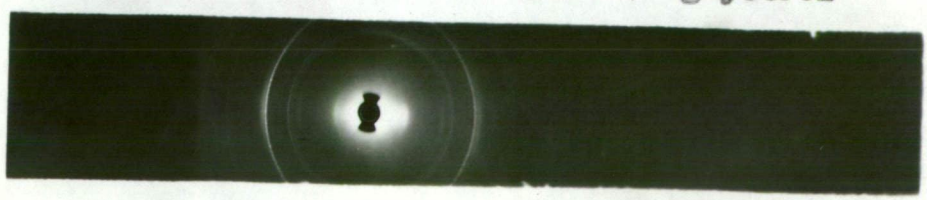
Whole sample (18) heated to 600°C



Aggregate less than 2 microns untreated

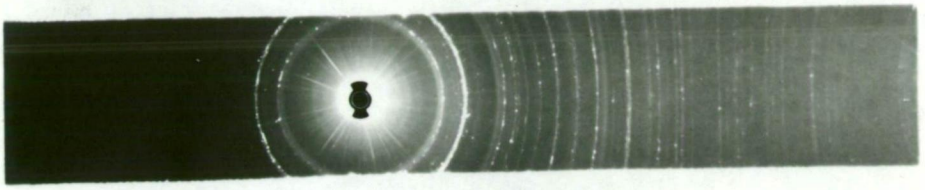


Aggregate less than 2 microns +glycerol

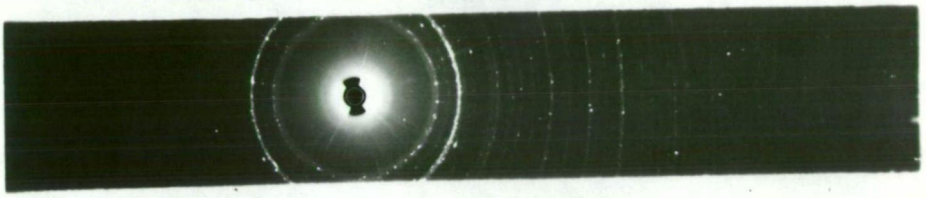


Aggregate less than 2 microns heated to 600°C

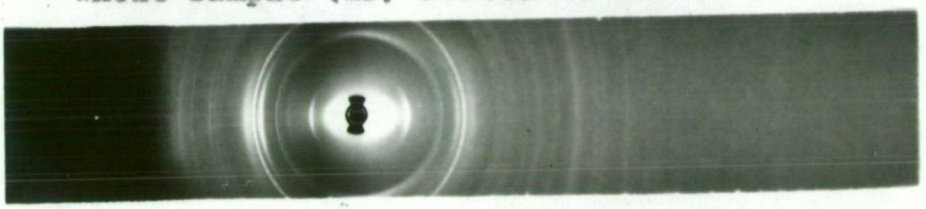
Whole sample (19) untreated



Whole sample (19) + glycerol



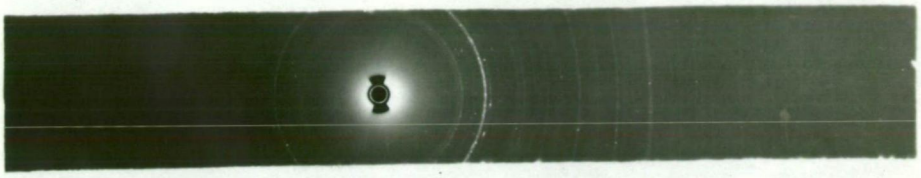
Whole sample (19) heated to 600°C



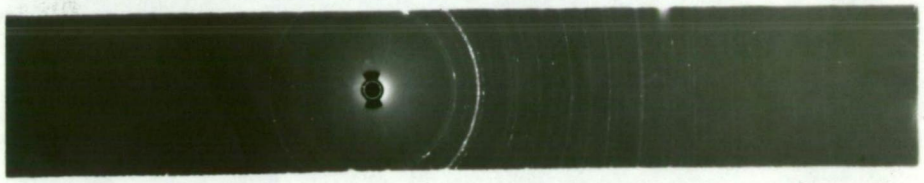
Aggregate less than 2 microns untreated

Aggregate less than 2 microns + glycerol

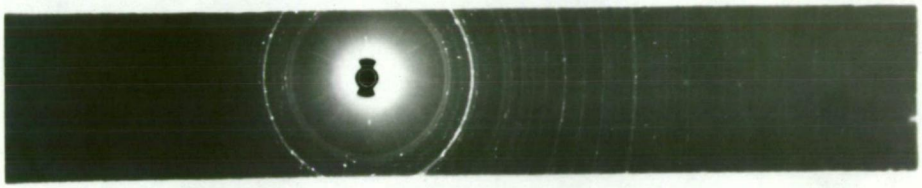
Aggregate less than 2 microns heated to 600°C



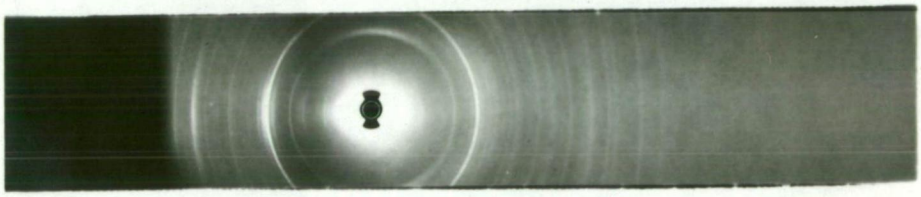
Whole sample (20) untreated



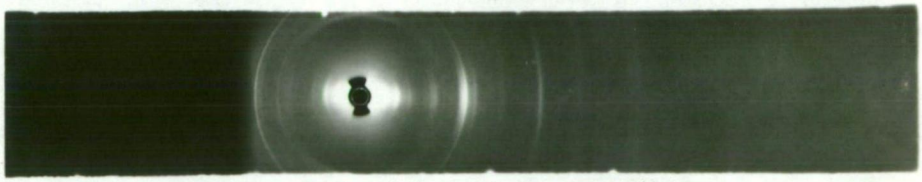
Whole sample (20) + glycerol



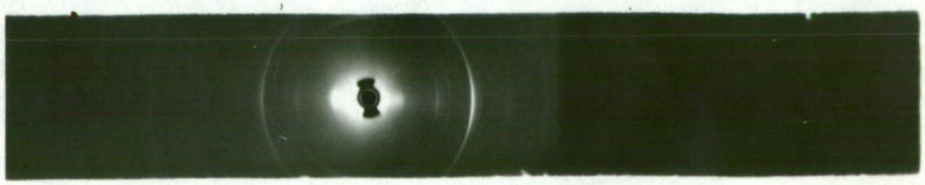
Whole sample (20) heated to 600°C



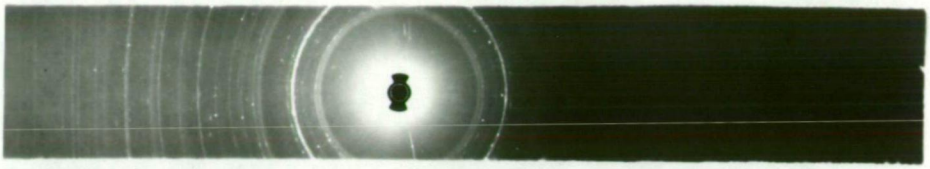
Aggregate less than 2 microns untreated



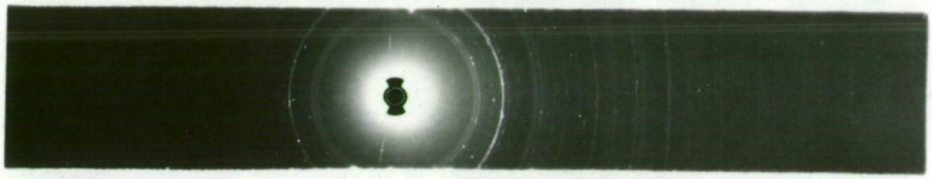
Aggregate less than 2 microns + glycerol



Aggregate less than 2 microns heated to 600°C

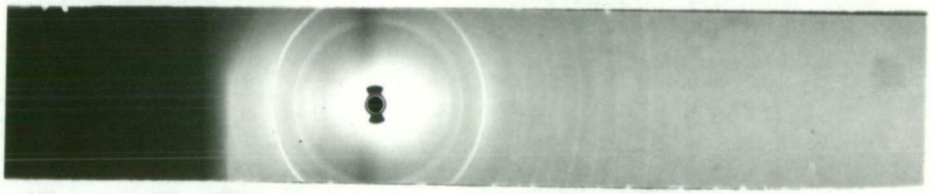


Whole sample (21) untreated

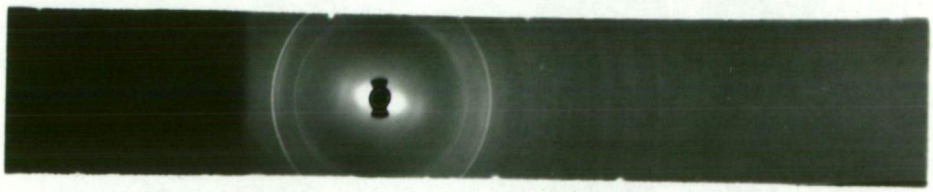


Whole sample (21) + glycerol

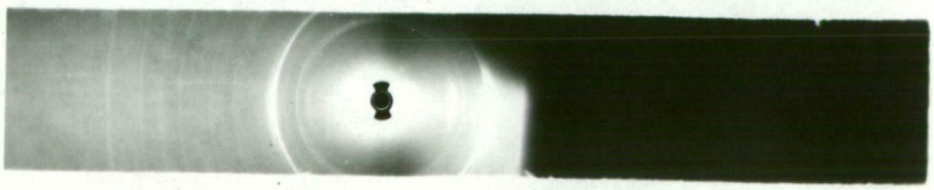
Whole sample (21) heated to 600°C



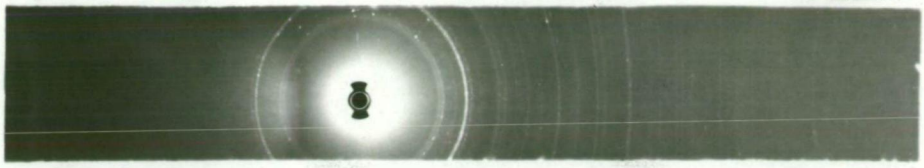
Aggregate less than 2 microns untreated



Aggregate less than 2 microns + glycerol

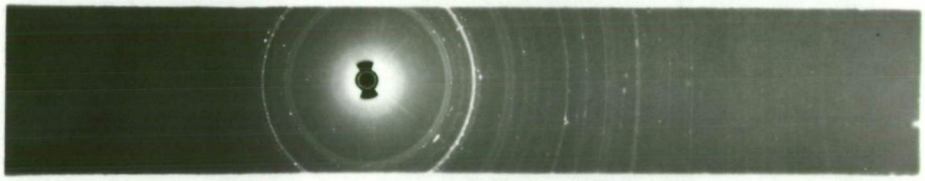


Aggregate less than 2 microns heated to 600°C

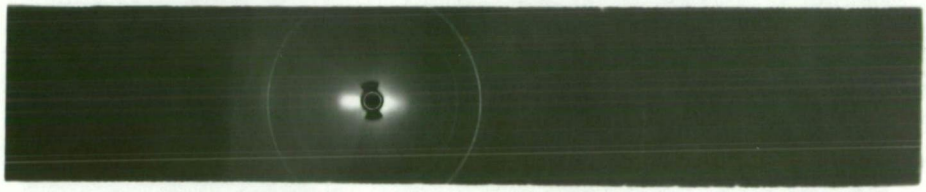


Whole sample (22) untreated

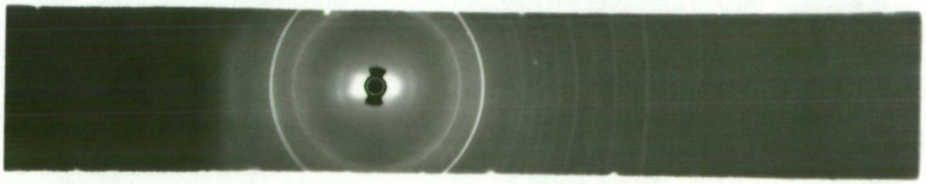
Whole sample (22) + glycerol



Whole sample (22) heated to 600°C

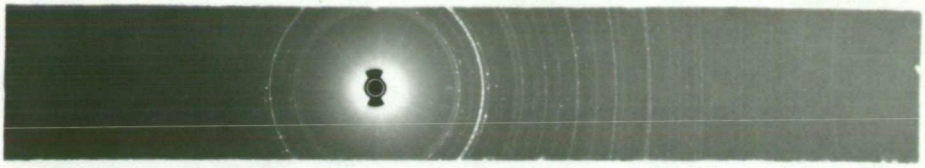


Aggregate less ttan 2 microns untreated

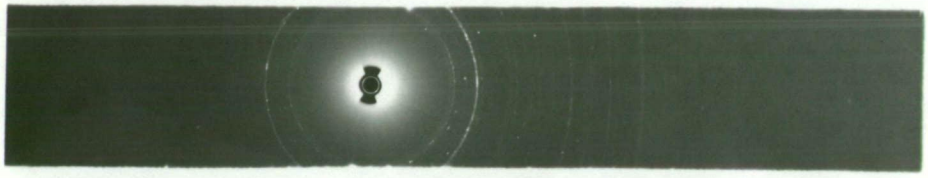


Aggregate less than 2 microns + glycerol

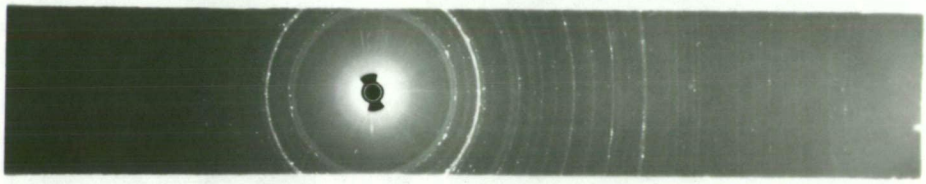
Aggregate less than 2 microns heated to 600°C



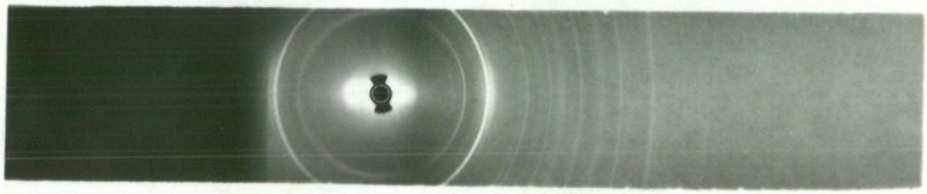
Whole sample (23) untreated



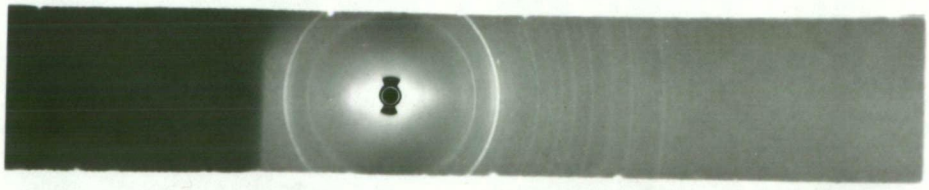
Whole sample (23) + glycerol



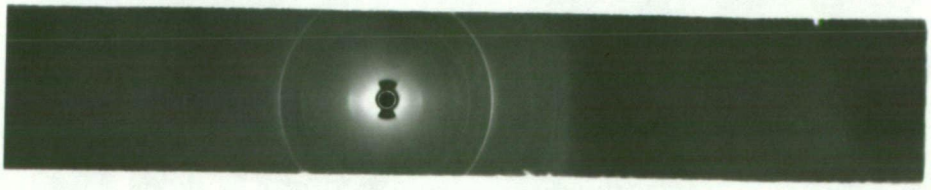
Whole sample (23) heated to 600°C



Aggregate less than 2 microns untreated



Aggregate less than 2 microns + glycerol



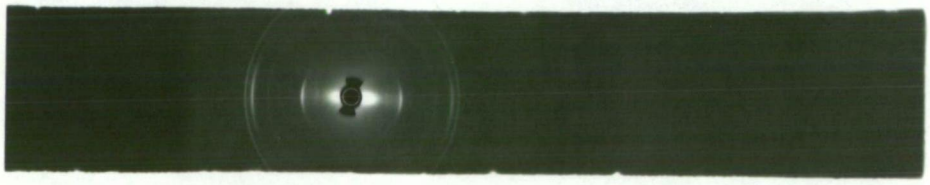
Aggregate less than 2 microns heated to 600°C

Whole sample (24) untreated

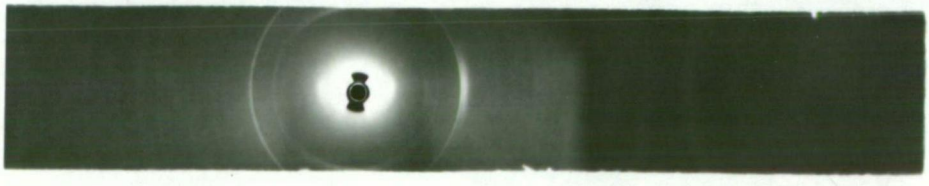
Whole sample (24) + glycerol

Whole sample (24) heated to 600°C

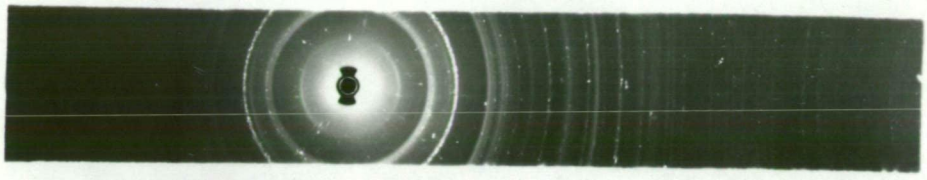
Aggregate less than 2 microns untreated



Aggregate less than 2 microns + glycerol

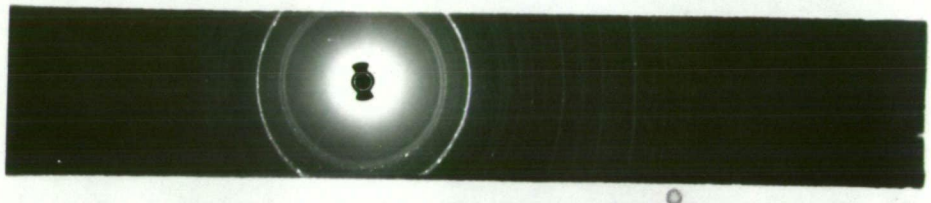


Aggregate less than 2 microns heated to 600°C



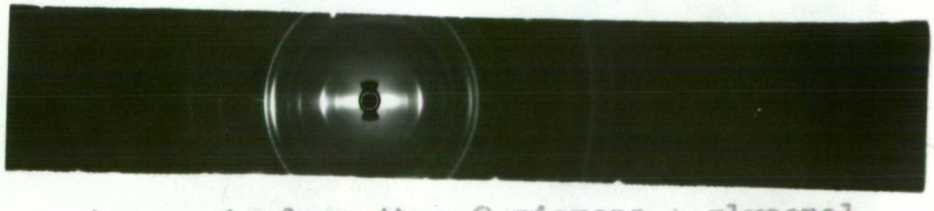
Whole sample (25) untreated

Whole sample (25) + glycerol

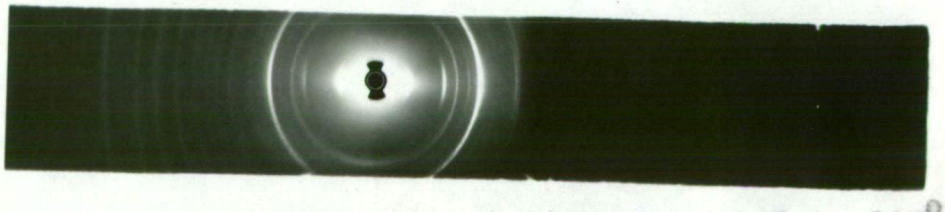


Whole sample (25) heated to 600°C

Aggregate less than 2 microns untreared

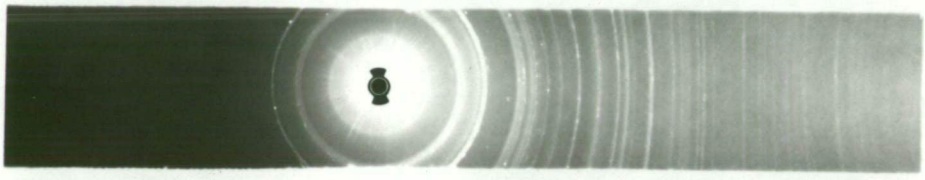


Aggregate less than 2 microns + glycerol

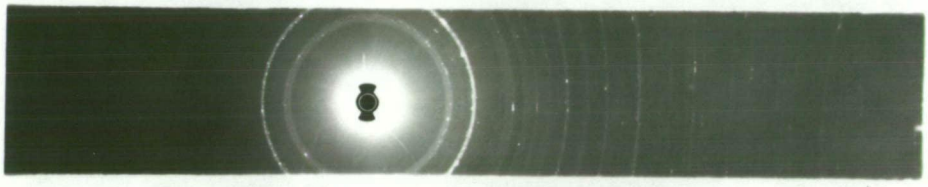


Aggregate less than 2 microns heated to 600°C

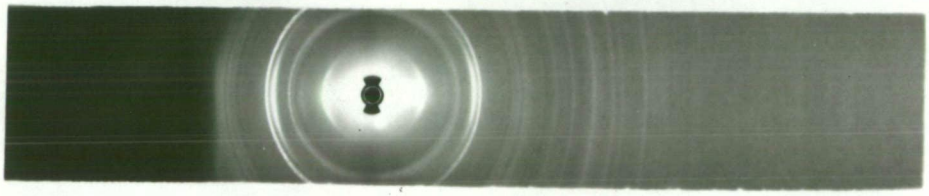
Whole sample (26) untreated



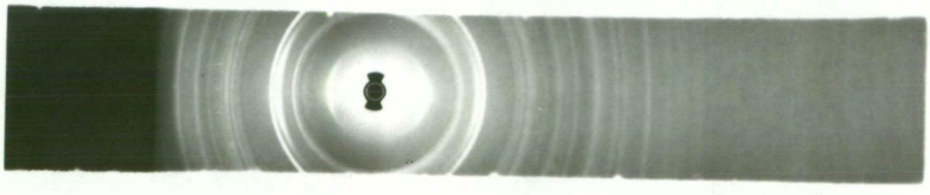
Whole sample (26) + glycerol



Whole sample (26) heated to 600°C



Aggregate less than 2 microns untreated



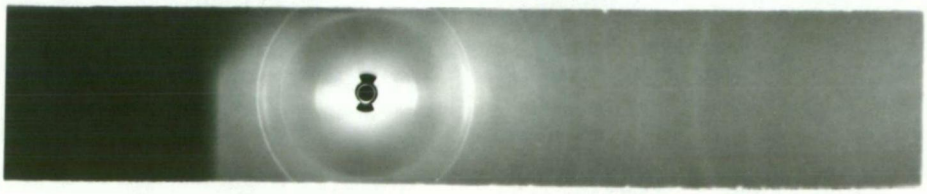
Aggregate less than 2 microns + glycerol

Aggregate less than 2 microns heated to 600°C

Whole sample (27) untreated

Whole sample (27) + glycerol

Aggregate less than 2 microns untreated

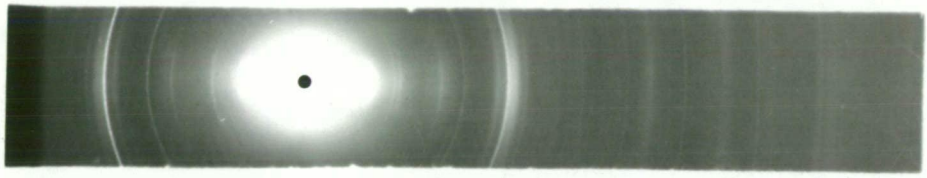


Aggregate less than 2 microns + glycerol

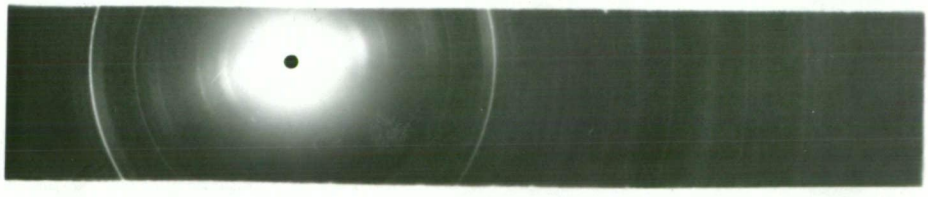
Aggregate less than 2 microns untreated (28)

Aggregate less than 2 microns + glycerol (28)

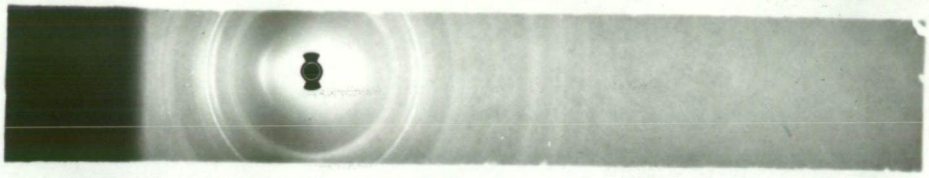
Photograph taken with Philips Camera



Aggregate less than 2 microns untreated (20)

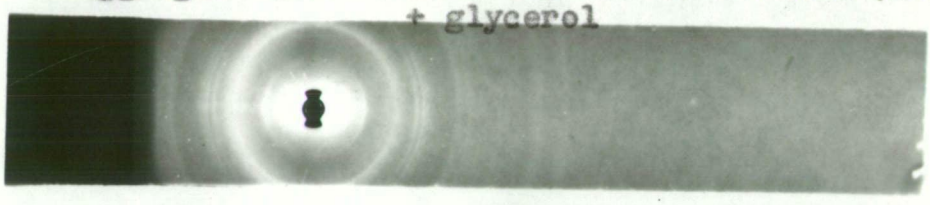


Aggregate less than 2 microns + glycerol (20)

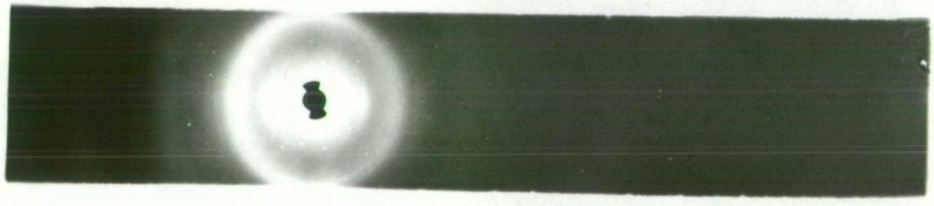


Aggregate less than 2 microns Li treated (1A)

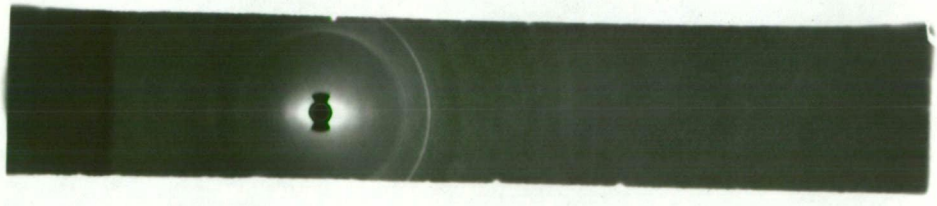
Aggregate less than 2 microns Li treated (1A) + glycerol



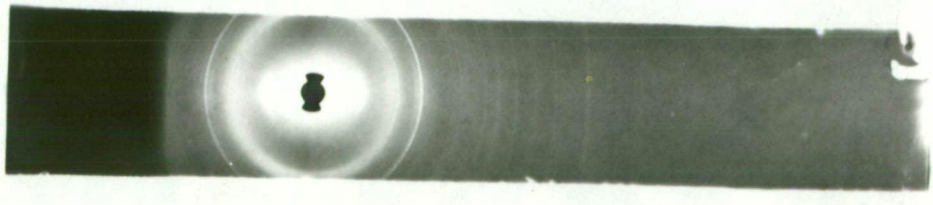
Aggregate less than 2 microns Li treated (2)



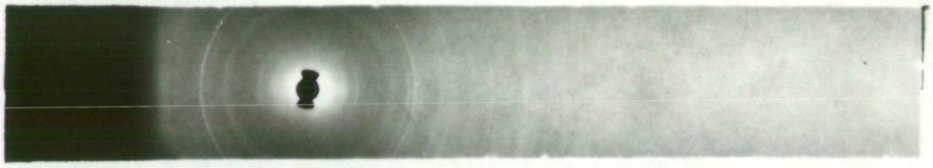
Aggregate less than 2 microns Li treated (2) + glycerol



Aggregate less than 2 microns Li treated (5)

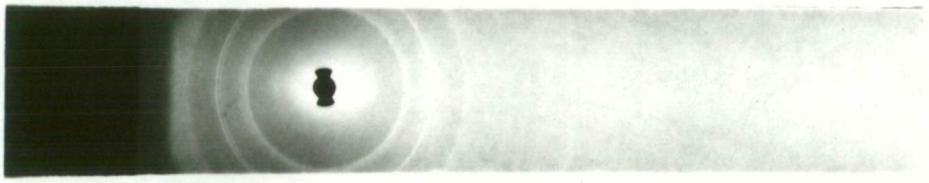


Aggregate less than 2 microns Li treated (5) + glycerol



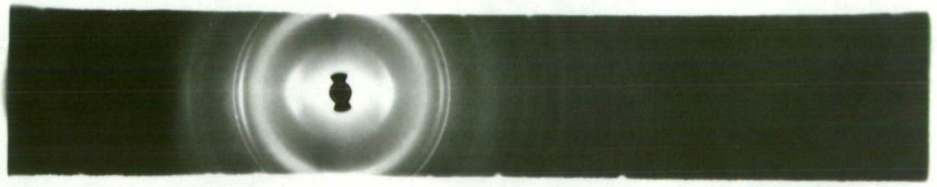
Aggregate less than 2 microns Li treated (10)

Aggregate less than 2 microns Li treated (10)
+ glycerol



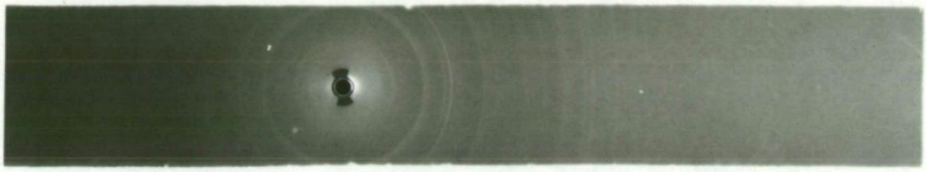
Aggregate less than 2 microns Li treated (16)

Aggregate less than 2 microns Li treated (16)
+ glycerol



Aggregate less than 2 microns Li treated (21)

Aggregate less than 2 microns Li treated (21)
+ glycerol



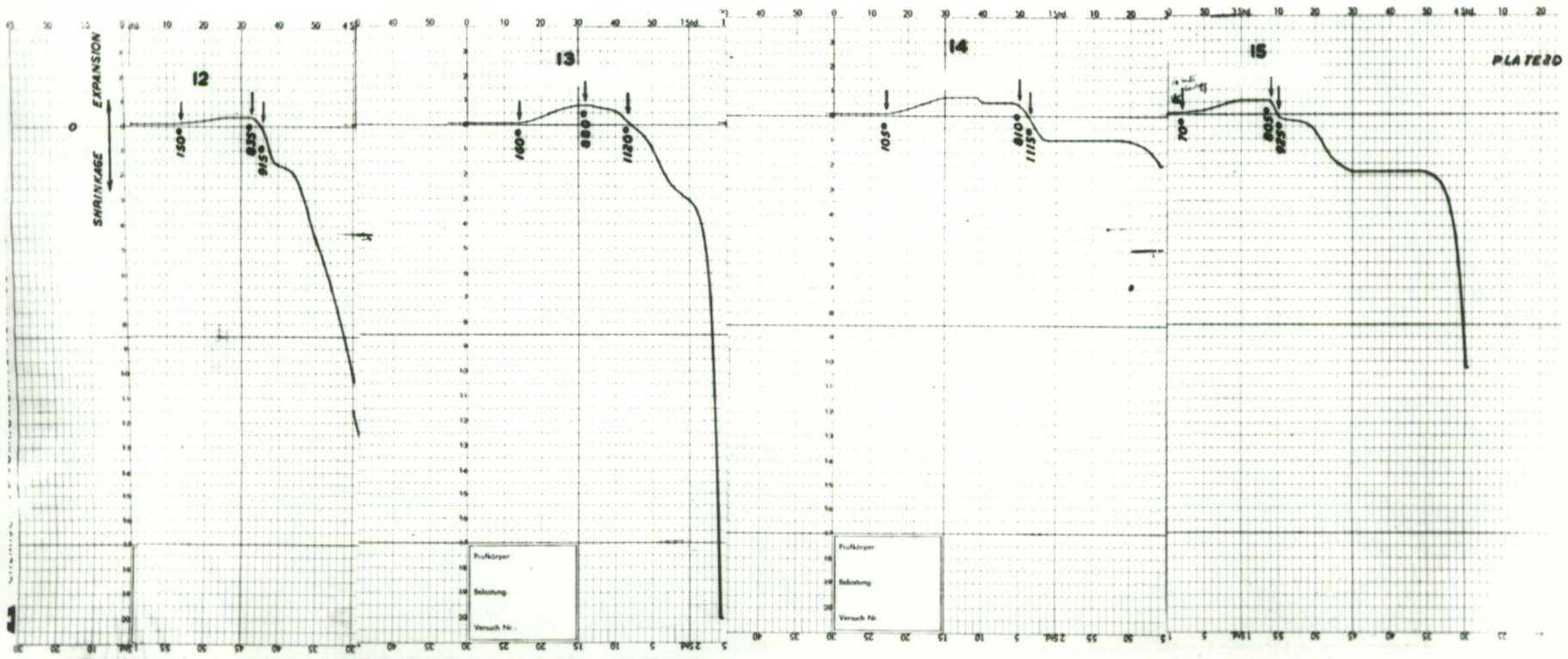
Clay fraction Li treated (19)

PLATE 2A

CHEMISCHES LABORATORIUM FÜR TONINDUSTRIE – BERLIN-FRIEDENAU
SHRINKAGE ⊖ EXPANSION
IA
1
2
3
845°
260°
910°
155°
1005°
375°
860°
260°
Prüfkörper:
Belastung:
Versuch Nr.:

PLATE 28
1095°
1020°
150°
1100°
940°
165°
1000°
910°
160°
905°
983°
195°
SHRINKAGE
EXPANSION
Prüfkörper
Belastung
Versuch Nr.
CHEMISCHES LABORATORIUM FÜR TONINDUSTR

CHEMISCHES LABORATORIUM FÜR TONINDUSTRIE – BERLIN-FRIEDENAU
SHRINKAGE EXPANSION
Prüfkörper:
Behandlung:
Versuch Nr.:
840°
775°
160°
900°
775°
140°
940°
870°
105°
680°
775°
PLATTE 22
11
10
9
8


EXPANSION
SHRINKAGE
12
13
14
15
150°
835°
915°
100°
880°
1120°
105°
910°
1115°
105°
850°
925°
Prüfkörper
Belastung
Versuch Nr.
PLATE 2D

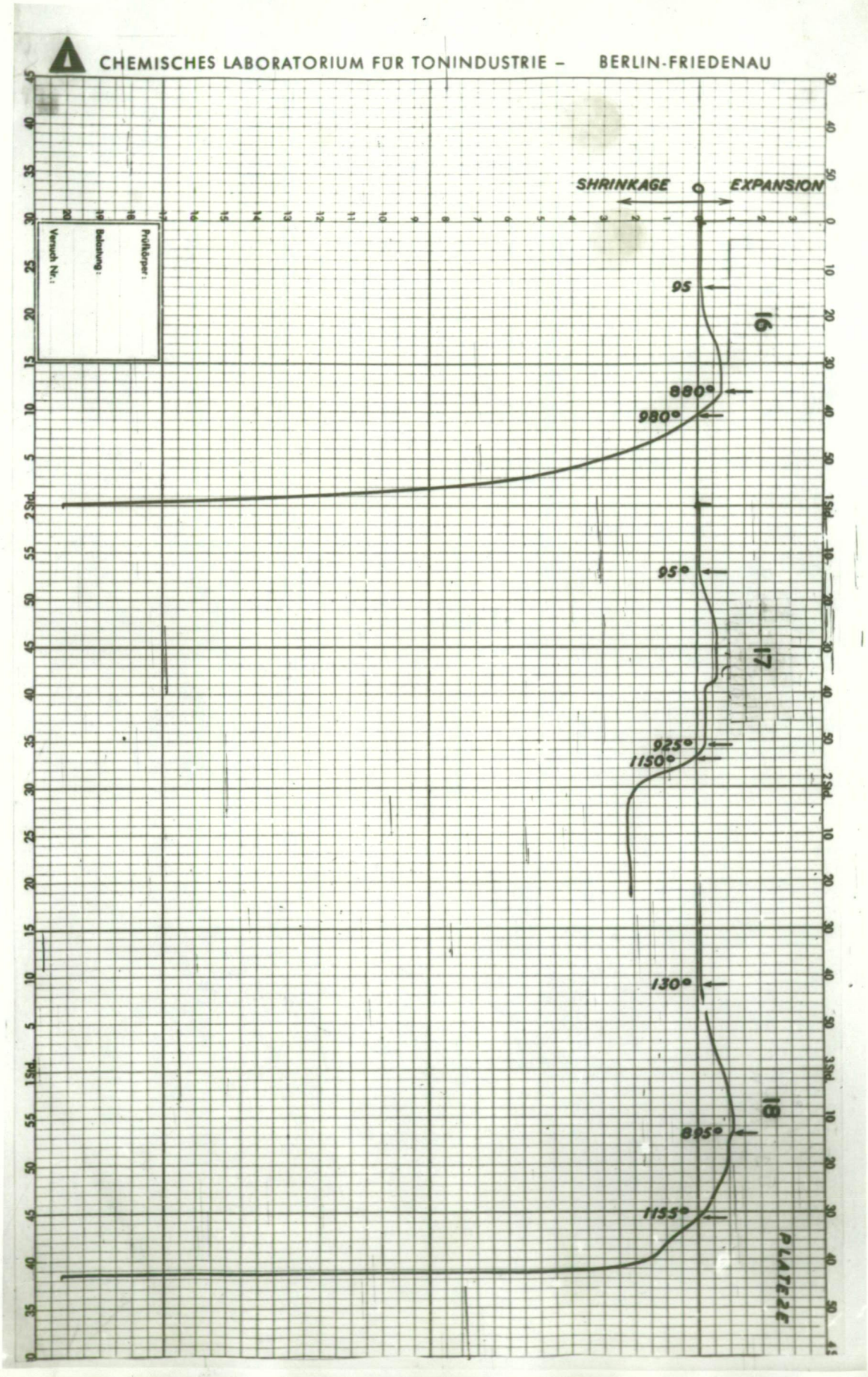

CHEMISCHES LABORATORIUM FÜR TONINDUSTRIE – BERLIN-FRIEDENAU
SHRINKAGE
EXPANSION
Prüfkörper:
Belastung:
Versuch Nr.:
95
880°
980°
95°
925°
1150°
130°
895°
1155°
16
17
18
PLATEZE

PLATE 2F
22
950°
840°
115°
21
950°
860°
160°
20
970°
860°
115°
19
1025°
880°
110°
SHRINKAGE
EXPANSION
Prüfkörper:
Belastung:
Versuch Nr.:

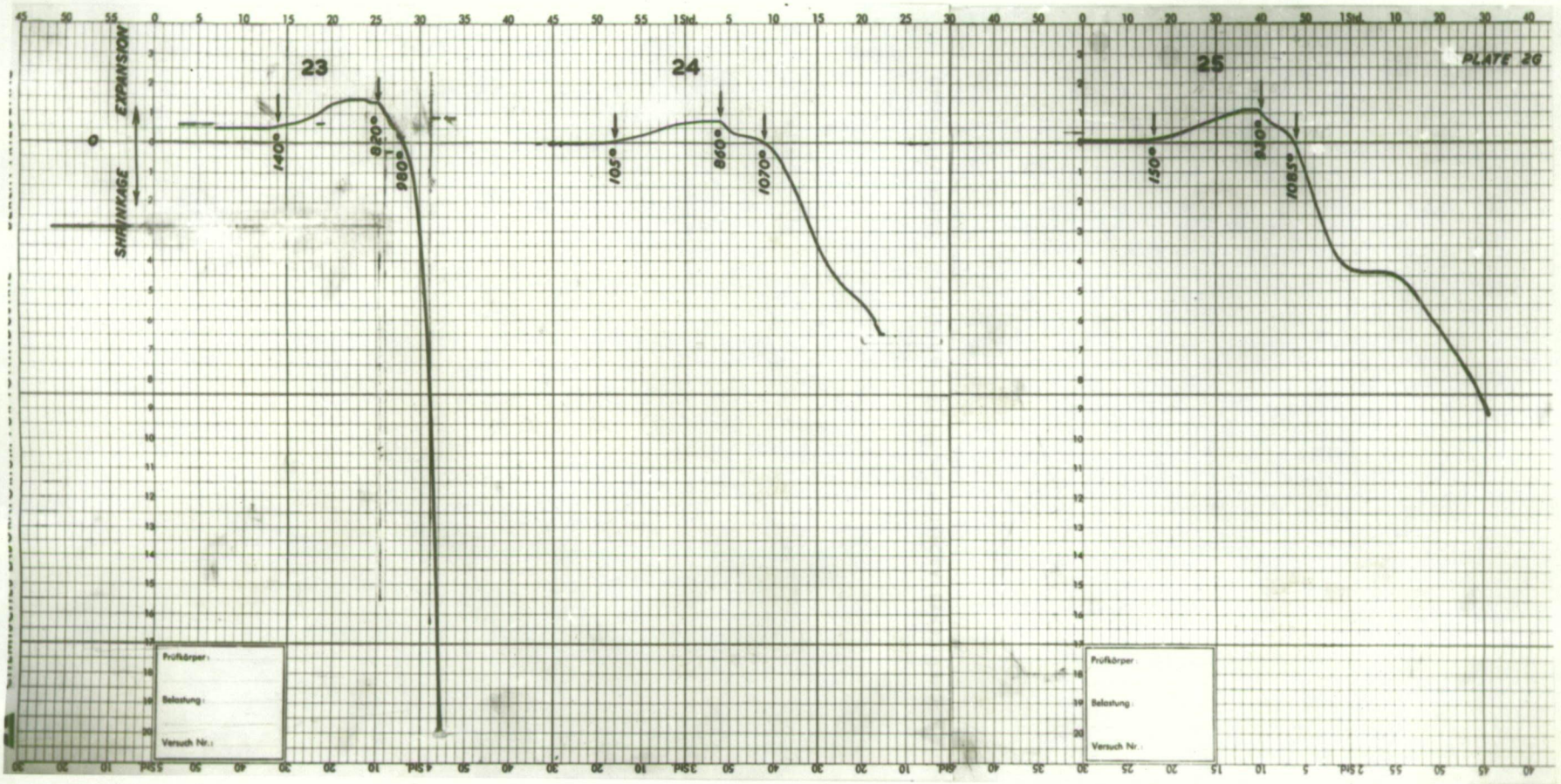
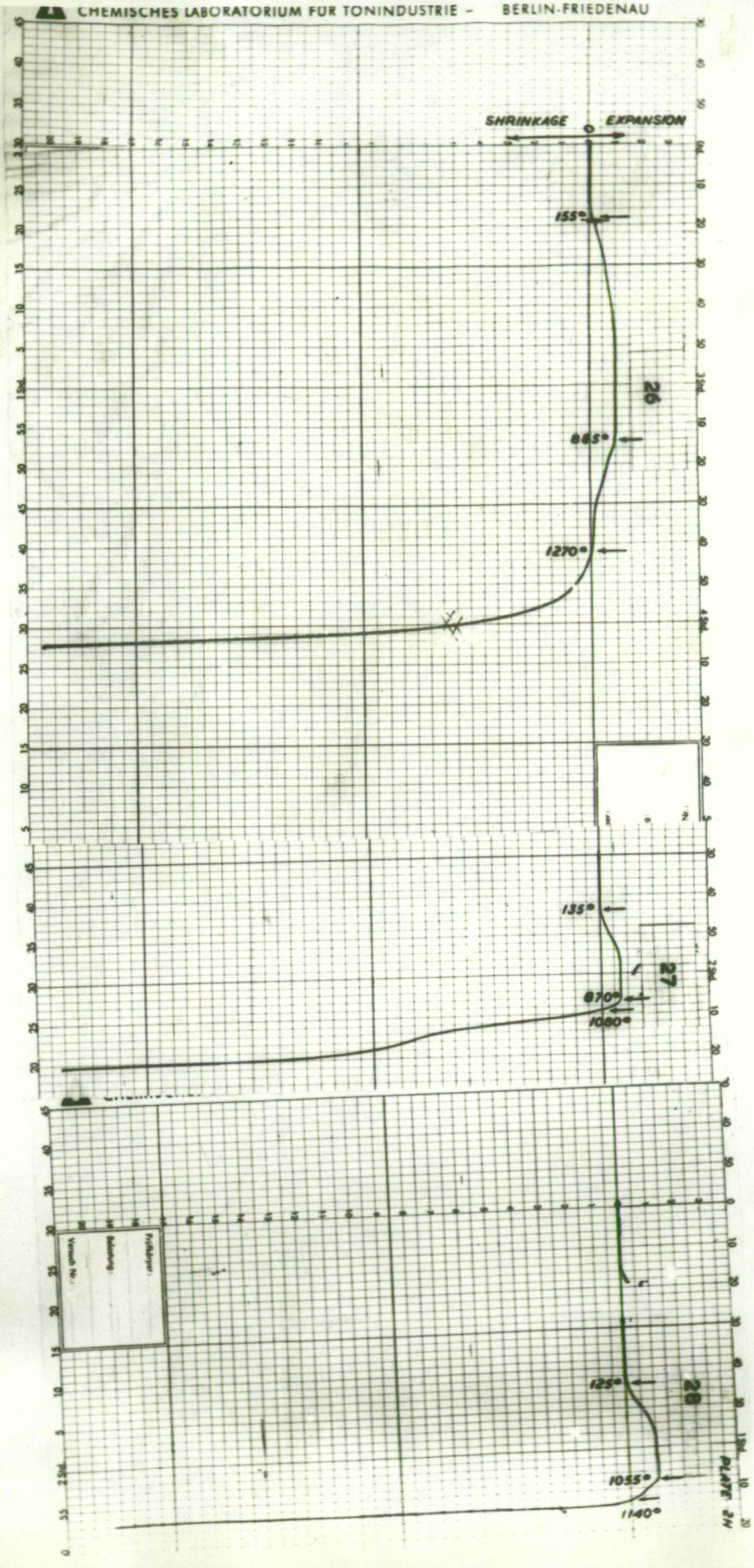

EXPANSION
SHRINKAGE
0
23
24
25
140°
200°
180°
105°
160°
107°
150°
200°
108°
Prüfkörper:
Belastung:
Versuch Nr.:
Prüfkörper:
Belastung:
Versuch Nr.:

PLATE 26


CHEMISCHES LABORATORIUM FÜR TONINDUSTRIE – BERLIN-FRIEDENAU
SHRINKAGE
EXPANSION
155°
665°
1270°
26
135°
870°
1080°
27
125°
1055°
1140°
28
PLATTE 2H